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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

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Rubber Division Activities

The Rubber Division of the American Chemical Society

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Sergeant-at-Arms.....L. V. COOPER

The Rubber Division Meeting in Rochester, N. Y., September 9 and 10, 1937

The meeting was held in the Powers Hotel, with two hundred and fifty in attendance. The following program was presented.

1. J. W. MacKay. Preparation and testing of latex compounds.
2. Thomas Midgley, Jr., Albert L. Henne and Mary W. Renoll. The protein from natural rubber and its amino acid constituents.
3. F. F. Lucas. Ultraviolet microscopy of Hevea rubber latex.
4. A. R. Kemp. Composition and structure of Hevea latex.
5. H. W. Starkweather and H. W. Walker. Softening agents in Neoprene.
6. H. W. Starkweather and H. W. Walker. Water-resistance of Neoprene.
7. E. W. Booth and J. W. MacKay. A comparison of the vulcanizing characteristics of smoked sheet and latex rubbers.
8. J. N. Dean. Electrical characteristics and aging properties of gutta-percha and balata.
9. R. L. Taylor and A. R. Kemp. Sorption of water by rubber.
10. E. T. Lessig. The Goodrich flexometer.
11. G. S. Haslam and C. A. Klaman. The T-50 test applied to zinc oxide compounds.

The Rubber Division banquet was held Thursday evening in the ballroom of the Powers Hotel, with three hundred and seventy-five in attendance. The banquet committee consisted of Vern Smithers, Chairman, Enos Baker, Treasurer, Art Kempel, Harry Seaman, H. E. Elden, Jack Hamilton. This committee is to be congratulated on the fine dinner and excellent entertainment provided.

The Rubber Division also wishes to thank the following companies for the financial support to make the excellent program possible:

Akron Standard Mold Company
American Zinc Oxide Company
Binney & Smith Company
Godfrey L. Cabot, Inc.
The Columbia Alkali Corporation
Continental Carbon Company
E. I. du Pont de Nemours & Company
General Atlas Carbon Company
General Dyestuff Corporation
The C. P. Hall Company
Keystone Filler & Manufacturing Co.
Midwest Rubber Reclaiming Company
Rubber Service Laboratories
Naugatuck Chemical
The New Jersey Zinc Sales Co., Inc.
Pequanoc Rubber Company
St. Joseph Lead Company
Titanium Pigment Corporation
United Carbon Company, Inc.
R. T. Vanderbilt Company, Inc.
C. K. Williams & Company
Wishnick-Tumpeer Chemical Company

At the general business session, officers were elected for 1938: Chairman, A. R. Kemp; Vice-Chairman, G. K. Hinshaw; Sergeant-at-Arms, L. V. Cooper; Secretary-Treasurer, C. W. Christensen; Executive Committee: H. L. Trumbull, F. H. Amon, L. W. Brock, Harold Gray, W. A. Gibbons, C. C. Davis, S. G. Byam.

The Secretary was instructed to write to the authors and editors of the new Monograph on "The Chemistry and Technology of Rubber" and thank them for their efforts.

R. H. Gerke, Chairman of the Crude Rubber Committee, reported to the Division.

The Chairman announced that it had been suggested by certain prominent chemists that the Rubber Division should pay honor to Charles Goodyear, the discoverer of the vulcanization of rubber, on the 100th anniversary of his discovery, during the calendar year of 1939. A general discussion followed and it was the consensus of opinion:

(1) That the Rubber Division is favorable to arranging a suitable program, preferably at a regular meeting of the A. C. S.

(2) That the Boston meeting is favored, providing the national officers of the A. C. S. prove to be agreeable to a plan of devoting the general meeting program exclusively to selected papers on rubber topics.

(3) That a standing committee be appointed now to make all arrangements for this meeting and to continue in office until such arrangements are consummated.

C. W. CHRISTENSEN, *Secretary*

Report of the Crude Rubber Committee, Rubber Division of the American Chemical Society

The Crude Rubber Committee met in Akron, Ohio, on June 4, 1937, at which time Harold Gray announced his resignation from the Crude Rubber Committee H. L. Trumbull appointed R. H. Gerke Chairman and L. M. Freeman, of The B. F. Goodrich Company, to replace Mr. Gray.

The Committee regrets to hear that Mr. Gray can no longer serve, and desires to congratulate him on his successful leadership.

At this meeting the final draft of the "Specifications for Testing the Variability of Normal and Concentrated Latex" was approved for distribution to the list of correspondents for further comment, and criticism before final approval, which is planned for 1938. The Committee hereby desires to thank officially all those who have kindly offered their services in coöperating in the preparation of the latex specifications.

W. T. L. ten Broock, of the Goodyear Rubber Plantations, was present and stated that the establishment of the standard recipe was a big advance. He also described the work of the Crude Rubber Committee in the Dutch East Indies. In connection with the standard recipe, work is in progress in the Far East in the evaluation of the Schopper machine *versus* the Scott machine, which has been used in this country for the purpose of testing rubber cured according to the recipe.

Three unfinished projects of the Crude Rubber Committee consist of a method for testing cleanliness, a method for preparing crude rubber samples for plasticity test, and a recipe which will be satisfactory for testing rubber with respect to variability of aging. While some data have been obtained on these subjects, it appears that these projects are of such a complex nature that it will be some time before satisfactory solutions can be worked out.

The Committee has received correspondence from Prof. Charles Dufraisse for the many kindnesses extended, especially by Mr. Gray, in arranging an itinerary for Mr. Jean Le Bras, and also by many other members of The Rubber Division who have coöperated in entertaining him in their plants and laboratories.

CRUDE RUBBER COMMITTEE,
R. H. GERKE (*Chairman*)
E. B. BABCOCK
G. A. SACKETT
J. C. WALTON
L. M. FREEMAN

New Books and Other Publications

Rubber, Its History and Uses. (Reprinted from the "Encyclopedia Americana.") By R. E. Powers. B. F. Goodrich Co., Akron, Ohio. 7 × 10 in. 8 pp.

Tracing the history of rubber from its discovery and primitive use by South American natives to present-day methods of production and research, Mr. Powers has done an excellent job. Written in an easy-to-read style, the author devotes considerable space to the development of the rubber manufacturing industry in this country, interspersing his historical notes with comment on the effect of each new important discovery and invention to the general public. A number of the more important uses of rubber are briefly discussed. [*The Rubber Age* of New York.]

Elasticity, Plasticity, and Structure of Matter. By R. Houwink. Published by University Press, Cambridge, England (also available from the Macmillan Company, New York City). $5^1/_2 \times 8^1/_2$ in. 376 pp. $6.00.

It is the expressed intention of the author to bring the three groups of workers interested in the study of elastic and plastic phenomena which take place upon the deformation of matter, *i. e.*, the physicist, the chemist, and the scientific technologist—into closer contact with each other, so that by the aid of an insight into the structure of matter they may seek to improve existing materials and discover new ones. By a series of comparative tests, he makes certain prophecies about the behavior of materials on deformation, on the basis of their respective structures, wherein (he claims) lies the key to the deliberate synthesis of materials with definite desired elastic and plastic properties. The book is divided into 13 chapters, one of which deals with rubber, gutta-percha and balata, discussing the chemical structure of rubber and its changes during vulcanization, the elastic behavior of rubber, molecular structure, "artificial" rubber, etc. The book has a complete author and subject index. In addition to the contents described, it also has a special chapter on "The Plasticity of Crystals," by W. G. Burgers. [*The Rubber Age* of New York.]

Twenty-Eighth Report of the Council. Rubber Growers' Association, Inc., 19 Fenchurch Street, London, E. C. 3, England. $6 \times 9^1/_2$ in. 58 pp.

Activities of the various committees of the R. G. A. during 1936 are reported in this book, that of the Propaganda Committee revealing that special attention has been paid to developing uses of rubber in agriculture, railways, the mining industry, textiles, and paints. The report reveals that in the future the activities of the Technical Research and Development of New Uses Committee will be absorbed into those of the recently organized British Rubber Research Board, brought into existence by the signatories of the International Rubber Regulation Committee. [*The Rubber Age* of New York.]

Dictionnaire Technique du Caoutchouc (Technical Rubber Dictionary). Compiled by L. Akobjanoff. Published by Revue Générale du Caoutchouc, 19 Boulevard Malesherbes, Paris, France. 5 × 7 in. 174 pp. 45 francs (approximately $1.75 at the current rate of exchange).

This handy little dictionary, published in English, French, German, and Russian, should find wide application in the rubber industry. It is not a dictionary in the full sense of the word, since it gives no definitions of the technical terms listed, but

will rather serve a useful purpose in enabling one to determine the English, French, German, or Russian equivalent of a technical term in any of the four languages. English words appear first, followed by French, German, and Russian equivalents, respectively. Each individual word is numbered. Since the English words are first, it is simple to locate them in their alphabetical sequence. French, German, and Russian words are alphabetically arranged in indices at the back of the book, with numbers referring the user to the English equivalent, or other language equivalent. [*The Rubber Age* of New York.]

Annual Survey of American Rubber Chemistry for 1936. By Webster N. Jones. Published by the Carnegie Institute of Technology, Pittsburgh, Penna. 6 × 9 in. 40 pp.

For a ten-year period (1925–1935) the "Annual Survey of American Chemistry" was published under the sponsorship of the National Research Council and was ably edited by Clarence J. West, director of the Council's research information division. Because of lack of financial resources, the Council discontinued its informational service and subsequently dropped its sponsorship of the annual survey. In order to insure continuity of the survey of American rubber chemistry, which was part of the N. R. C.'s annual survey, and with the hope that future publication will be resumed, the City of Pittsburgh sponsored the current study, which was edited by W. N. Jones, assisted by workers furnished by the Works Progress Administration. The current study follows the style of the former annual reviews. It discusses developments which occurred in 1936 in the fields of crude rubber, rubber chemicals, testing methods, reclaiming, latex and rubber dispersions, hard rubber, synthetic rubber, rubber derivatives, etc. A complete list of references is also included. [*The Rubber Age* of New York.]

Manual de la Industria de la Goma (Manual of the Rubber Industry). Edited by Luis Pascual Mejias Lopez. Published by La Goma, Calle de Moncada, 4, Barcelona, Spain. 7 × 10 in. 362 pp. 25 Pesetas, 15 Centimos to foreign countries, postage-paid (approximately $3.15).

Consisting of fifty chapters and a subject index, this book represents a summary of the various branches of the rubber industry. Chapters are devoted to different species of rubber plants, cultivation, theory and methods of vulcanization, vulcanization accelerators, dissolution of rubber, analyzing crude rubber, testing methods, reclaimed rubber, solvent recovery, factice, manufacturing processes, pneumatic and solid tires, development of rubber machinery, manufacture and application of hard rubber, synthetic rubber, etc. The book is illustrated throughout, with pictures of rubber machinery liberally sprinkled through those sections devoted to manufacturing processes. It includes a number of suggested formulas for the production of various products. This manual is described by the publishers as being the first original book written in Spanish on the subject of rubber. [*The Rubber Age* of New York.]

Synthetic Rubber. By W. J. S. Naunton. Published by Macmillan & Co., Ltd., St. Martin's Street, London, England. $5^1/_2 \times 8^1/_2$ in. 162 pp. 7s. 8d. (approximately $2.00 at the current rate of exchange).

The first book devoted solely to the subject of synthetic rubber since the publication of the monograph by S. F. Schotz (published by Reinhold) in 1926, this volume differs from the other in that it not only deals with the chemical aspects of the

subject, but also the technical and economic sides. As the author states in his preface, the subject is handled "from as wide an angle as possible, so as to interest both the layman who is interested in the history of man's attempts to produce rubber synthetically and the more technically minded reader." The book contains 9 chapters, in addition to a lengthy introduction by Professor Sir William J. Pope (University of Cambridge). The chapters are devoted to the history, economic aspect, chemistry, physics, technology, and applications of synthetic rubber. Other chapters treat of the borderland between rubber and resins, synthetic rubber latex, and the future outlook of the material. The technical section of the work is devoted almost entirely to Neoprene, du Pont's chloroprene rubber. [*The Rubber Age* of New York.]

Uses of Rubber in Commercial Horticulture. By Alexander Hay. Published by the Rubber Growers' Association, Inc., 19 Fenchurch St., London, E. C. 3, England. 16 pp. $5\frac{1}{2} \times 8\frac{1}{2}$ in.

Sixth in the series of rubber and agriculture bulletins prepared for the Rubber Growers' Association by the author, its agricultural liaison officer, this latest bulletin deals with the use of rubber in horticulture, particularly pneumatic-tired equipment. A rubber-slotted pad used as a tree tie and the use of rubber fittings for cloches (in cultivation of vegetables under glass) are also described and illustrated in the bulletin. [*The Rubber Age* of New York.]

The Reactions of Pure Hydrocarbons. By Gustav Egloff. Published by the Reinhold Publishing Corporation, 330 West 42nd Street, New York City. 6×9 in. 900 pp. $16.75. (A. C. S. Monograph No. 73.)

This monograph represents an attempt to correlate all the research work on the reactions of pure hydrocarbons being carried on by scientific organizations throughout the world. How successful this attempt was can best be realized from the 1500 references cited and the more than 50 pages of author and subject indices. The book covers the reactions of pure hydrocarbons resulting from thermal, catalytic, photochemical and electrical treatment, and is the most exhaustive work on the subject to date. It correlates, explains, and criticizes the mass of work done on the subject by approximately 1200 different investigators. The author, director of research for the Universal Oil Products Company, Chicago, is well qualified to offer such criticism. Rubber chemists will be particularly interested in the discussion of the non-catalytic treatment of rubber, which occupies a section of the last chapter of the book. [*The Rubber Age* of New York.]

Handbook of Chemistry. (Second Edition.) Compiled and edited by Norbert Adolph Lange. Published by Handbook Publishers, Inc., Sandusky, Ohio. $5\frac{1}{2} \times 8$ in. 1802 pp. $6.00.

This second edition is larger than the first, has been completely revised and brought up to date, contains many new tables, and includes 250 pages of mathematical data which were compiled by Richard Stevens Burington, Assistant Professor of Mathematics at the Case School of Applied Science. Like the first edition, this volume is intended as a reference volume for all requiring ready access to chemical and physical data used in laboratory work and manufacturing. The book contains a comprehensive, cross-referenced index. One section is devoted to the chemical resistance of rubber and to the physical properties of hard and soft rubber. [*The Rubber Age* of New York.]

[Reprinted from Journal of the American Chemical Society, Vol. 59, No. 4, pages 706–707, April, 1937.]

Natural and Synthetic Rubber

XVII. The Separation of Sol Rubber and Gel Rubber[1]

Thomas Midgley, Jr., and Albert L. Henne

The sol rubbers, on which reliable physical and chemical measurements have been made, have been prepared either by fractional precipitation[1] from a mixture of benzene and alcohol, or by slow diffusion in absolute ethyl ether.

The separation of sol from gel rubber by diffusion assumes that the components can be separated from one another like sugar from sand and disregards the possibility that sol and gel rubbers may be mutually soluble in each other. If this latter condition actually exists, then the diffusion may only be expected to produce a two-phase, three-component system in equilibrium, and the relative amounts of sol and gel rubbers in the sol phase should be determined and not assumed. The same general reasoning applies to the fractional precipitation method of separation. Thus there is no "absolute" method of determining the relative quantities of sol and gel rubbers in any sample.

However, the relative efficiencies of separation by these two methods may be evaluated by preparing samples of "sol" rubber by each method and then attempting a further separation of each of these samples by the other method. This has been done with the following results.

Samples of sol rubber were prepared by fractional precipitation from sprayed latex rubber and were allowed to diffuse in ether. They dissolved rapidly and completely. They were quantitatively recovered unchanged from the ether by evaporation at reduced pressure. Also 30 g. of sprayed latex was allowed to diffuse in absolute ether, yielding 24 g. of soluble and 6 g. of insoluble material. The insoluble portion was leathery, rich in nitrogen; it was not analyzed further. The 24 g. of soluble material was recovered from the limpid ether solution by evaporation at reduced pressure, then subjected to fractional precipitation from a mixture of alcohol and benzene, with the following results:

Fractions	A_0	A_1	A_2	A_3	A_4	A_5	B
Amount, g.	3	6	1	1.5	1	0.5	10.5

One-half gram was lost during the operation. The A_0 fraction contained the so-called "acetone soluble" portion of natural rubber, since it was recovered by the evaporation of the benzene-alcohol mixture after completion of the fractionation. The A_1 fraction was found free of nitrogen, but not free of rubber degraded by oxidation, as it had a glossy appearance and gave 0.06% oxygen by the active hydrogen method[2] instead of 0.02 or 0.03% which is normal for good samples. This is not surprising, as it has always been found that two and sometimes three successive precipitations are needed to remove all traces of such oxidized material. Fractions A_2 to A_4 were typical high-grade sol samples. Fraction A_5, which was very small and obtained with considerable difficulty, was obviously a mixture of A and B. Fraction B, the insoluble part, proved to be nitrogen free. In view of this last unexpected result, B was subjected to another fractionation, which removed only

a small amount of impure A, amounting to about 2 g., and left a little more than 8 g. of a substance which was called BB. The characteristics of this BB fraction were: no nitrogen; 4.65% oxygen by combustion; 1.48% oxygen by active hydrogen measurement; slow solubility in benzene; extremely slow solubility in ether; no "leathery" feeling, no "tackiness" and no resemblance whatever to rubber degraded by oxidation. The high oxygen content of this material may safely be assumed to be due to an impurity.

The viscosities of the several fractions were measured in 0.23% solutions in benzene at 20°. The viscosities expressed in C. G. S. units $\times 10^3$ were:

Benzene	A_1	A_2	A_3	A_4	BB
6.47	12.40	17.20	17.30	17.20	21.03

The low viscosity of A_1 is due to the accumulation therein of rubber degraded by oxidation. A_2 to A_4 are good samples of sol rubber. Their viscosities compare favorably with those recorded for thrice refractioned sol rubber (17.70) or twice refractioned rubber (17.40 to 17.65) prepared in this Laboratory.

These results indicate quite clearly that a single diffusion of rubber into ether is insufficient completely to separate sol from gel rubber. They also show that while there is no absolute criterion by which the fractional precipitation method may be judged, it is decidedly more efficient than the ether diffusion method.

Summary

Sol rubber prepared by a single diffusion in ether can be separated into two components by fractional precipitation, whereas sol rubber prepared by a single fractional precipitation completely diffuses in ether, thus indicating the superiority of the fractional precipitation method as a means of preparing sol rubber.

References

[1] *J. Am. Chem. Soc.*, **53**, 2733 (1931); RUBBER CHEM. TECH., **4**, 547 (1931).
[2] *Ibid.*, **57**, 2318 (1935); RUBBER CHEM. TECH., **9**, 74 (1936).

[Reprinted from Industrial and Engineering Chemistry, Vol. 29, pages 793–799, July, 1937.]

Colloidal Structure of Rubber in Solution

S. D. Gehman and J. E. Field

The Goodyear Tire & Rubber Company, Akron, Ohio

THE type of colloidal behavior exhibited by rubber solutions presents the nature of the colloidal structure in solution as a complicated problem with nearly as many aspects as there have been fields of experimentation. Most of the methods of colloidal research have been applied, at least to some extent, to rubber solutions. A satisfactory scientific understanding of the structure will eventually require a convergence of the points of view arrived at by these different methods. Each source of independent information about the structure imposes its limitations upon the possibilities. In this work the writers have relied principally upon what is essentially a new and untried method of colloidal research as applied to rubber solutions—a study of the intensity and depolarization of the transversely scattered light. In addition to securing this new information, they have attempted to show how the results are related to those obtained from the method which has been of greatest general use in the past—namely, viscosity measurements.

Light-scattering measurements have been used for many years in the study of suspensions and colloidal systems such as gelatin solutions (*13*, *14*), agar-agar sol-gel transitions (*5*), gum mastic (*18*), and numerous other colloidal suspensions. No systematic study of the light scattered by rubber solutions seems to have been made.

Optical Apparatus and Method

The optical system for making measurements of the relative intensity and depolarization of the transversely scattered light is illustrated in Figure 1:

The system is mounted in a darkroom. The source of light, *S*, is a 1000-candle-power Pointolite tungsten arc. The lens system, *L*, *L'*, is focused to give a beam of approximately parallel light, the angular divergence from the axis being 2.5°. The source and lenses are mounted on an optical bench in a light-tight housing, cooled by a fan. The beam is limited by diaphragms with rectangular openings, so that it has a cross section of 0.5 × 2 cm. at the light-scattering cell. *F* is a yellow filter (Corning No. 351) which makes the light more homogeneous and removes any blue light that might cause fluorescence. It also protects the solutions. The right-angle prism, *G*, reflects part of the light beam into one entrance of a Martens polarizing

photometer, T. This reflected beam is reduced in intensity by a neutral glass filter, F', and then serves as a standard of comparison. This arrangement eliminates errors due to variations in the brightness of the source. P is a Polaroid disk which can be introduced in such a way as to polarize the incident beam with the direction of vibration either vertically or horizontally, as may be desired. B is a small steel box provided with appropriate windows. It is filled with water in order to minimize light reflections from the glass cell containing the rubber solution. When the cell is placed in the box in position R, the scattered light enters the right-hand entrance of photometer T. This polarizing photometer consists of a double-image prism arranged so that half of the field is illuminated by the vertically polarized component from the right-hand entrance, whereas the other half of the field is illuminated by the horizontal component from the left-hand entrance, as it is mounted. The field is then matched by rotation of a Nicol prism. The ratio of the intensities of the two beams is given by the square of the tangent of the angle of rotation from the zero position. In practice, two

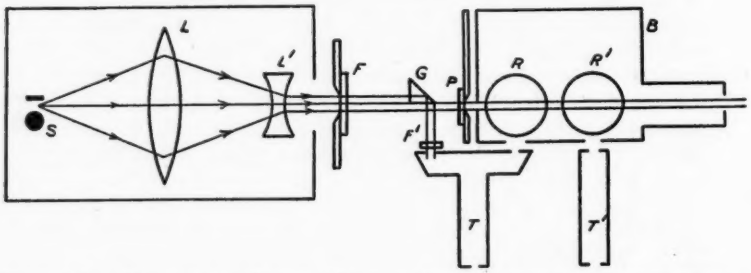

FIGURE 1. DIAGRAM OF OPTICAL SYSTEM FOR MEASURING RELATIVE INTENSITY AND DEPOLARIZATION OF TRANSVERSELY SCATTERED LIGHT

match points are read on either side of the zero position and the angle taken as half of the difference of the readings.

The description of the photometer shows that it is designed for use with unpolarized light. Since the scattered light is polarized, photometer T gives the relative intensity of only the vertical component, as it is mounted. T', however, is a single-entrance polarizing photometer so that the tangent squared of the angle of the Nicol, in this case, gives the ratio of the intensities of the horizontal and vertical components, the cell being placed at R' to secure the reading. Knowing the ratio of the horizontal and vertical components, and the relative intensity of the vertical component, the relative total intensity can be calculated. The equipment thus makes possible a complete analysis of the scattered light for any state of polarization of the incident beam.

The intensity of the light scattered by solutions of purified rubber is so low that great care is required in matching the fields, and the eye must be completely dark-adapted. The sensitivity of the eye decreases for low intensities (*12*). Sufficient readings were taken so that the average could be duplicated to within a few tenths of a degree of arc of the photometer dial.

Light-Scattering Cell and Solutions

To make the light-scattering and viscosity measurements desired, a technic was required that would fulfill the following requirements:

1. Eliminate motes and dust from the solvent.
2. Protect the solutions from air.
3. Permit the concentration of a solution to be changed by the addition of dust-free solvent without exposure to air.
4. Provide for viscosity measurements on the identical solutions used for light-scattering measurements.

These needs were met by the use of the combined viscometer and light-scattering cell shown in Figure 2:

It consisted of a spherical and a tubular unit joined by a connecting tube. The bulb of the spherical unit has a volume of about 35 cc. The tubular unit is graduated and has a volume of about 60 cc. Light-scattering measurements were made on the solution when in the spherical bulb, the bulb being immersed in the water bath previously described. To make viscosity measurements, an Ostwald type viscometer is attached as shown. The capillary diameter was 0.4 mm. The viscometer may be filled from the top, without any interchange of fluid between the sphere and tube, by tilting the entire unit. The whole cell was immersed in a water thermostat at 30° C. for the viscosity measurements.

When making up a solution, a weighed amount of rubber was introduced into the bulb and the solvent poured into the tube. The system was evacuated with a water pump, and some of the solvent was boiled off and sealed. The bulb containing the rubber was placed in an acetone–solid carbon dioxide mixture, and the solvent was allowed to distill over from the tube without boiling. This procedure eliminates all motes and dust from the solvent (*1*, *21*). At such low temperatures the rubber does not readily go into solution, so that it and the bulb and viscometer could be washed several times with dust-free solvent before the final distillation which filled the bulb. Several days were sometimes required for the rubber to go into solution, during which time the cell was kept in a refrigerator. After light-scattering and viscosity measurements were made at one concentration, the solution could be diluted by pouring a measured volume of solution into the tube and distilling back the same volume of solvent. In this way light-scattering and viscosity curves could be obtained as a function of the concentration without exposure of the solutions to air and dust. At the end of the process, values are obtained for the pure solvent.

The rubber used throughout this work was petroleum-ether diffusion rubber obtained from acetone-extracted pale crepe rubber by a continuous extraction process such as described by Pummerer (*27*). Petroleum ether was selected as the extracting fluid rather than ethyl ether because it seemed to preserve the gel structure of the crepe rubber better. The apparatus used for the extraction is shown in Figure 3, which is self-explanatory. Rubber stoppers, protected by aluminum foil, were used for the connections. The extracted rubber was precipitated with acetone and dried *in vacuo*. It was always handled with the greatest care to avoid contamination with dust.

FIGURE 2. VISCOMETER AND LIGHT-SCATTERING CELL

Theory

Before presenting the results, it will be advantageous to give a brief résumé of the theoretical background of the method of light-scattering measurements as applied to the investigation of colloids. This will greatly facilitate the discussion of the results and is necessary in order to understand them.

Four types of light scattering should be considered in the case of light scattering by rubber solutions:

1. Scattering by colloidal particles.
2. Scattering due to local density fluctuations (*6*, *31*).
3. Scattering due to composition fluctuations (*6*).
4. Scattering due to the random orientation of anisotropic molecules (*29*).

By fluctuations are meant statistical variations from the average values due to the thermal agitation of the molecules.

Rayleigh worked out the procedure for calculating the light scattered by small, spherical particles in suspension. His fundamental equation is well known and has frequently been the basis for light-scattering studies of colloids. A modification of this equation by Putzeys and Brosteaux (*28*) is given here:

$$\frac{Ir^2}{E} = \frac{9\pi^2}{2\lambda^4 N}\left(\frac{\mu_1^2 - \mu_2^2}{\mu_1^2 + 2\mu_2^2}\right)^2 \frac{6(1+\rho)}{6-7\rho}\,\phi^2 g M \qquad (1)$$

where I = intensity of transversely scattered light
E = intensity of incident beam
r = distance at which I is observed
λ = wave length of light

N = Avogadro's number
μ_1 = refractive index of the protein
μ_2 = refractive index of the medium
ϕ = specific volume of the protein
g = concentration, grams per cc.
M = mol. weight of large molecules assumed responsible for scattering
ρ = ratio of horizontal to vertical component in scattered light

Equation 1 was used by Putzeys and Brosteaux for the determination of the relative molecular weights of proteins from measurements of the intensity of the light scattered by water suspensions of the proteins. The factor $6(1 + \rho)/(6 - 7\rho)$ is a correction factor introduced by Cabannes to take care of the observed depolarization due to imperfect spherical symmetry.

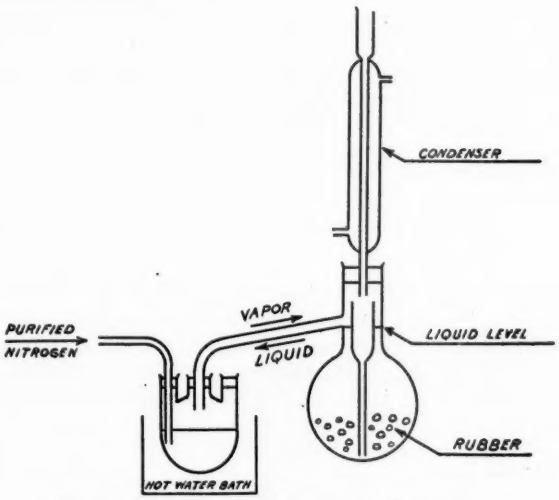

FIGURE 3. RUBBER EXTRACTION APPARATUS

Putzeys and Brosteaux compared the intensity of the light scattering from a series of proteins in water solution, the molecular weights of which were available from the ultracentrifuge; they concluded that the intensity of the scattered light was directly proportional to the molecular weights and was not influenced by solvation, ion concentration, or aggregation.

Rayleigh's equation is limited to small, spherical particles in random arrangement. Calculations have also been made for the scattering from larger spherical particles (*2*, *3*, *32*). Gans (*8*) elaborated the theory to apply to differently shaped particles. He adopts the more general assumption that the particles are ellipsoids of the revolution. Depending upon the ratio of the axes, these particles in the limiting cases can be rods, spheres, or plates.

The assumptions for Gans' theory are:

1. All the scattering is due to particles having a different refractive index from the medium.
2. The particles are small compared to the wave length of light but large enough to be assigned a definite index of refraction and geometrical form.
3. The distance between the particles is large compared to the wave length of light.
4. The particles are in random orientation and distribution.

Under these limitations there can be practically no question of the validity of the theoretical work, but there is considerable question as to how closely a rubber solution fulfills these conditions.

Gans defines the depolarization of the scattered light, incident light unpolarized, as

$$\theta' = \frac{J_2}{J_1 - J_2} \tag{2}$$

where J_2 = intensity of horizontally vibrating component in scattered light
J_1 = intensity of vertical component

The quantity ρ in Equation 1 is J_2/J_1, so that

$$\theta' = \frac{\rho}{1 - \rho} \tag{3}$$

Gans showed that the depolarization is a function of the concentration and used θ'_0 to indicate the depolarization, extrapolated to zero concentration—i. e., the depolarization for a single particle. θ'_0 is dependent on the particle shape. From Gans' equations, the following values have been derived for θ'_0:

Particle Form	θ'_0
Rods	$\frac{(m^2 - 1)^2}{m^4 + 8m^2 + 21}$
Spheres	0
Plates	$\frac{2(1 - m^2)^2}{7m^4 + 6m^2 + 2}$

where $m = \frac{\mu_1}{\mu_2} = \frac{\text{refractive index of particle}}{\text{refractive index of medium}}$

According to these equations it should be possible to determine the general shape of the colloidal unit from the depolarization of the scattered light. Thus, for a solution of rubber in ether, $m = 1.13$ and we compute the following values for θ'_0:

Particle Form	θ'_0
Rods	0.00236
Spheres	0
Plates	0.00734

It is apparent from the expressions for θ'_0 that the depolarization increases as m deviates from unity.

If θ is the depolarization of the scattered light for vertically polarized incident light, Gans has shown that:

$$\theta' = 2\theta \tag{4}$$

If ρ_u is the depolarization ratio for unpolarized incident light, ρ_v for vertically polarized incident light, then from Equations 3 and 4,

$$\rho_u = \frac{2\rho_v}{1 + \rho_v} \tag{5}$$

Furthermore, it follows from Gans' theory that if the incident light is horizontally polarized, the scattered light will be unpolarized; i. e., $\rho_h = 1$.

Gans' equations show that the intensity of the scattered light is proportional to V^2, if V is the volume of the particle, and is rather insensitive to particle shape.

For $m = 1.13$ as before, we calculate the following relative intensities of the light scattered by single particles of equal volume, the incident light being unpolarized:

Particle Shape	Relative Intensity
Rods	1.02
Spheres	1.00
Plates	1.03

When the particles are large compared to the wave length of light, Gans' theory does not apply and the intensity of scattered light decreases as the particle size increases for the same concentration (*10*).

Krishnan (*15*, *16*, *17*) developed a new method for investigating structure in liquids, glasses, etc., by means of light-scattering measurements. It surmounts to some extent the limitation of previous theory to particles small compared to the wave length of light. The method utilizes measurements of ρ_u and ρ_v which have already been defined. In contrast, ρ_h is the ratio of the vertical to the horizontal components in the scattered light for horizontally polarized incident light. Gans' theory shows that $\rho_h = 1$ and this value is actually observed for ordinary liquids and for suspensions of particles which are small compared to the wave length of light. Krishnan discovered, however, that for some systems ρ_h is definitely less than one, since the scattering units, which he regards as molecular clusters, are large. He derived the relation

$$\rho_u = \frac{1 + \frac{1}{\rho_h}}{1 + \frac{1}{\rho_v}} \tag{6}$$

Equation 6 reduces to Equation 5 when $\rho_h = 1$. Hence the deviation of ρ_h from unity is an indication of the size of the scattering units. To a first approximation, $2\rho_v/(1 + \rho_v)$ represents the portion of ρ_u due to the anisotropy of the scattering units. The portion due to the finite size of the units is, then, $\rho_u - (2\rho_v)/(1 + \rho_v)$ which Krishnan calls $\Delta\rho_u$.

The theory of the Krishnan effect, the deviation of ρ_h from unity, was further developed by Gans (*9*) and Vrkljan and Katalinić (*33*). Their analysis shows that the effect also depends upon the geometrical form of the scattering units. A large unit with spherical symmetry still gives $\rho_h = 1$. For rod-shaped scattering units with appropriate assumptions about the optical anisotropy, Vrkljan and Katalinić give for the length of the unit:

$$l^2 = \left(\frac{1}{\rho_h} - 1\right)\frac{84}{k^2} \qquad (7)$$

where $k = \dfrac{2\pi}{\lambda'}$

λ' = wave length of light in the system

Theory is still inadequate to explain completely the optical properties of liquids, but the causes of the discrepancies with classical theory are beginning to be recognized and dealt with (*23*). The modern view of the structure of a liquid must be taken into account. It can no longer be considered that the positions and orientations of the molecules are random. On the contrary, the molecules of a liquid form quasi-crystalline or cybotactic groups, small compared to the wave length of light, which are anisotropic for anisotropic molecules. The hindered rotation of the molecules and the anisotropy of the electric forces must be introduced into the calculations to explain the depolarization of the scattered light and the optical properties of pure liquids. Evidence for the existence of cybotactic groups is also available from other fields (*4*, *20*, *34*).

For rubber solutions these factors must be very important in their influence upon the light scattering, and it seems probable that the ultimate explanation of the results will be in these terms rather than in the terms generally applicable to a colloidal suspension. Light-scattering measurements afford the possibility of the introduction of newer and more powerful theoretical concepts for the explanation of the properties of rubber solutions and lyophilic colloids than the comparatively simple mechanical pictures of macromolecules or discrete, solvated micelles usually advanced in connection with the colloidal description of such solutions. In the application of the theory of hindered rotation and cybotactic groups to rubber solutions, difficulties will be encountered due to the fact that the units are large compared to the wave length of light and that there is every reason to

suppose that the scattering units show a size distribution rather than uniformity.

Dependence of Scattered Light Intensity on Solvent

Figure 4 shows the relative intensity of the scattered light from one per cent by volume solutions of rubber in various solvents. The points are measured values. The curve is obtained by computing the factor $\left(\frac{\mu_1^2 - \mu_2^2}{\mu_1^2 + 2\mu_2^2}\right)^2$ in Equation 1 for each solution and dividing by the value of the factor for the ethyl ether solution. This gives computed values rela-

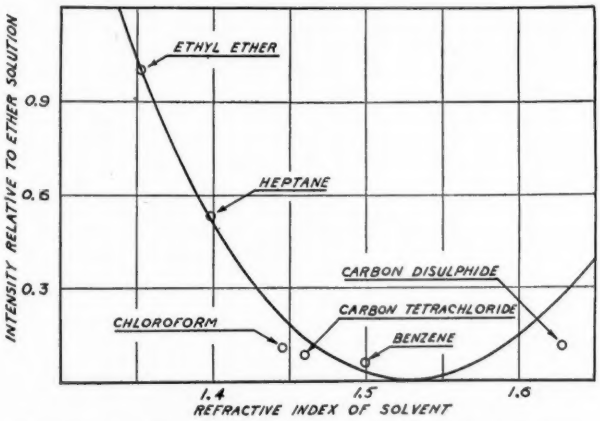

FIGURE 4. RELATIVE INTENSITY OF SCATTERED LIGHT FROM ONE PER CENT BY VOLUME SOLUTIONS OF RUBBER IN VARIOUS SOLVENTS

tive to the ethyl ether solution. As previously pointed out, this intensity factor is practically independent of the particle shape, so that if the scattering units were of the same size in the different solvents and the type of scattering conformed to Gans' assumptions, the curve should coincide with the experimentally observed values.

Although the intensity for the heptane solution is on the curve, the other solvents show marked departures. The scattering for the carbon disulfide, carbon tetrachloride, and chloroform solutions falls below the curve, whereas that from the benzene solution is greater than expected relative to the ether solution. The same facts are indicated even more strikingly by the following relative intensities observed for 10 per cent by volume solutions of petroleum-ether diffusion rubber:

Solvent	Relative Intensity of Scattered Light	
	Calculated	Observed
Ethyl ether	1.000	1.000
Heptane	0.507	0.643
Benzene	0.016	0.139

Thus the relative intensity of the scattering of ether and heptane solutions might indicate a reasonable conformance to the conditions for the application of Gans' theory of the scattering by colloids and a reasonably identical scattering unit. For the other solvents used, either the scattering units or the mechanism of the scattering process appears to be different and the difference in the index of refraction of the solvent and the rubber is no longer the controlling factor. The intensity of the scattering for chloroform, carbon tetrachloride, benzene, and carbon disulfide tends to be the same. It seems improbable that the scattering units would be

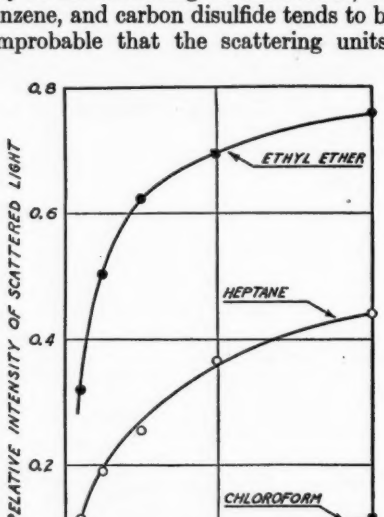

FIGURE 5. RELATIVE INTENSITY OF SCATTERED LIGHT FOR VARIOUS SOLVENTS

different in just the degree necessary to compensate for the differences in refractive index. Much more probable is the possibility that the light scattering arises from a structure of oriented groups which is essentially the same for these solvents, the mechanism of the scattering being analogous to that occurring for a pure liquid or liquid solution rather than to that from a colloidal suspension. We consider this a sounder point of view than to conclude from Figure 4 that the scattering units in chloroform, carbon tetrachloride, and carbon disulfide solutions are smaller and those in benzene larger than in the ether solution or vice versa, depending upon how large the units are compared to the wave length of light. More definite information about the size of the scattering units can be secured from the depolarization measurements which will be discussed later.

Dependence of Scattered-Light Intensity and Viscosity on Concentration

Curves showing the relative intensity of the scattered light for various solvents used are given in Figures 5 and 6. Petroleum-ether diffusion rubber was used in both cases but was extracted from different batches of acetone-extracted crepe rubber and showed a large variation in the solution viscosity.

The specific viscosity of a 0.25 per cent solution in ethyl ether of the rubber used for the data of Figure 5 was 1.12 and that for the rubber in the case of Figure 6 was 2.02, nearly twice as great.

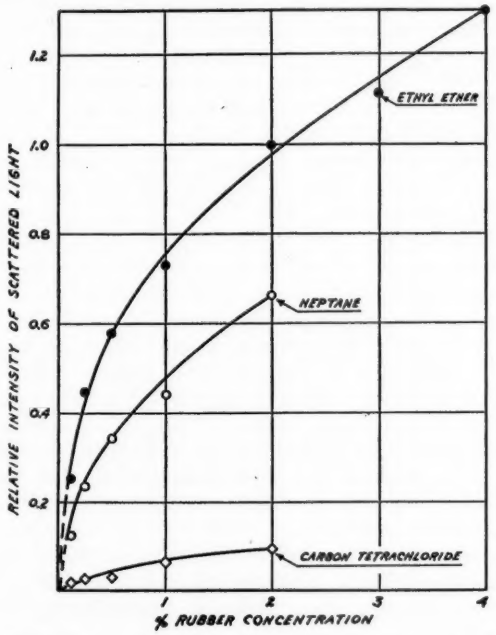

FIGURE 6. RELATIVE INTENSITY OF SCATTERED LIGHT FOR VARIOUS SOLVENTS

The curves of Figure 5 illustrate the point previously made that the light-scattering properties of rubber solutions show marked differences from ordinary lyophobic colloidal suspensions. The intensity of the light scattering for the rubber solutions is not, in general, proportional to the concentration. The writers do not believe that the flattening of the curves at the higher concentrations in Figure 5 was influenced to any measurable extent by light absorption and secondary scattering which serve to flatten this type of curve for more opaque suspensions. The writers failed to measure any light absorption by means of a Weston photoelectric

cell mounted to receive the incident beam after passage through the solutions.

The curves in both Figures 5 and 6 for ethyl ether and heptane solutions show a distinct change in slope at about 0.4 per cent by volume concentration which may be indicative of a change in structure at this concentration, somewhat corroborating the views of Staudinger. Unfortunately, the intensity of the light scattered from carbon tetrachloride and chloroform solutions is so low that for these solvents we cannot say much about the form of the curve at low concentrations. The flattening of the intensity curves shows that the tendency of the rubber solutions to scatter light like a pure liquid is most pronounced at the higher concentrations. Another possible interpretation is that the size of the scattering unit changes with the concentration. As the concentration is increased, the structure should approximate that of solid rubber and it is conceivable that the intensity of the scattered light would actually decrease if the curves were extended far enough.

The viscosity curves in Figure 7 show an entirely different character from the light-scattering intensity curves. The viscosity measurements were made on the identical solutions used for the light-scattering measurements shown in Figures 4 and 5. The viscosity curves are convex towards the concentration axis, whereas the intensity curves are concave.

There is some disagreement in the literature upon the relative viscosities of benzene and carbon tetrachloride solutions of rubber, and the meagerness of the data has been pointed out by Philippoff (*26*). Philippoff also summarized the mathematical treatment of the viscosity-concentration curve. The explanations of McBain (*19*) for the viscosity of colloidal solutions are closely related to some of the ideas arrived at from our work.

Figure 8 shows the interesting relation found to exist between the dielectric molecular polarization of the solvents and the viscosity. The dielectric molecular polarization is given by

$$P_{e.m} = \frac{K-1}{K+2}\frac{M}{d} \qquad (8)$$

where K = dielectric constant
M = molecular weight
d = density of solvent

Ostwald previously pointed out the connection of the dielectric polarization with various colloidal phenomena (*24*, *25*), and it has been used in studies of the swelling of rubber (*7*), but the writers believe this to be the first time that such a direct relation to the viscosity of rubber solutions has been shown. The direct implication is that electrical forces are concerned

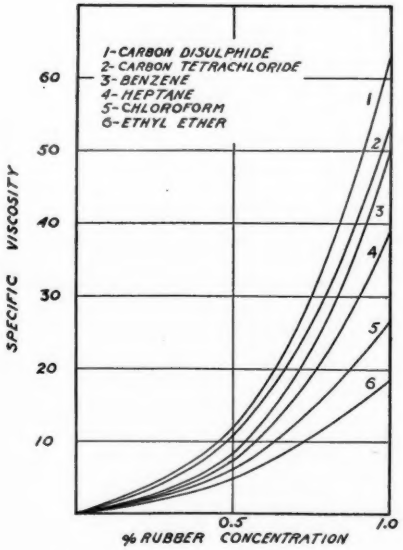

FIGURE 7. VISCOSITY CURVES

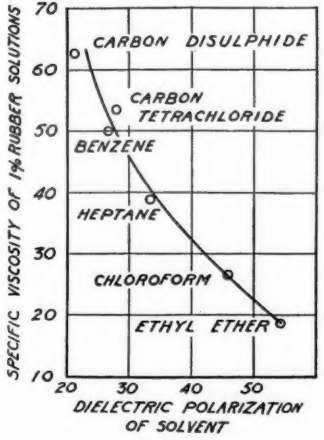

FIGURE 8. RELATION BETWEEN DIELECTRIC MOLECULAR POLARIZATION OF SOLVENTS AND VISCOSITY

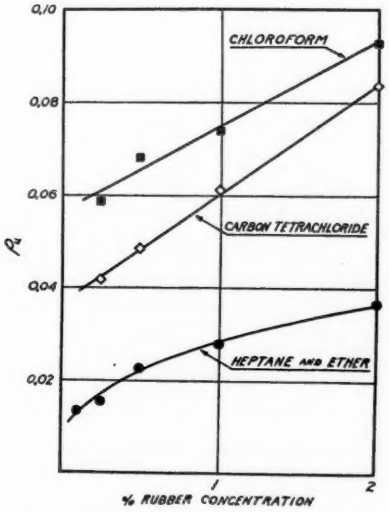

FIGURE 9. MEASURED VALUES OF ρ_u

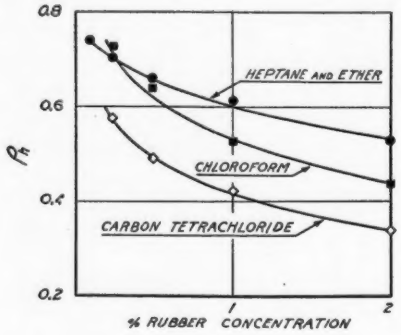

FIGURE 10. MEASURED VALUES OF ρ_h

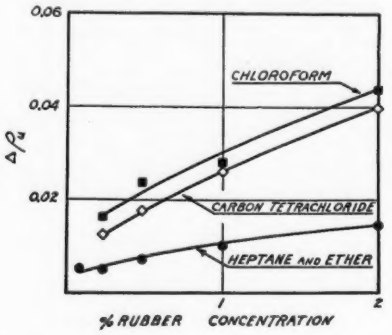

FIGURE 11. MEASURED VALUES OF $\Delta\rho_w$

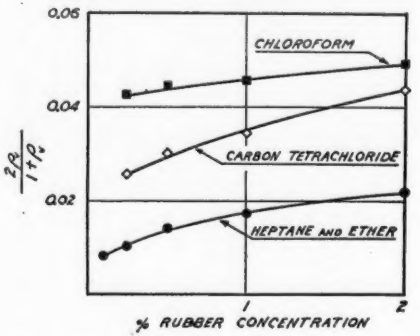

FIGURE 12. PLOT OF $2\rho_w/(1 + \rho_w)$

in the viscosities of the solutions. An older interpretation of this same function of the dielectric constant was that it represented the actual volume occupied by the atomic nuclei of the liquid (*11*).

Depolarization of Light Scattered by Rubber Solutions

The depolarization of the scattered light was measured for the solutions of which the intensity of scattered light is given in Figure 5. For suspensions which conform to the assumptions of Gans' theory, definite conclusions can be drawn concerning the particle shape from the depolarization of the scattered light. It was previously shown that Gans' theory predicts a limiting value, θ'_0, for a rubber-ether solution of 0.0024 if the particles are rods, 0 if they are spheres, and 0.0073 if they are plates. Figure 9 shows the measured values of ρ_u, from which we compute from Equation 3, $\theta'_0 = 0.01$, which is larger than the theoretical values. Furthermore, Gans' theory predicts that for the same particle θ'_0 will decrease as the difference in refractive index between medium and particle diminishes, whereas we find that a carbon tetrachloride solution of rubber shows a larger depolarization than the ether solution. This is definite proof that the rubber solutions do not conform to the assumptions of Gans' theory. To secure information about the structure from the depolarization of the scattered light, it is therefore necessary to adopt the analysis of Krishnan and measure, in addition to ρ_u, ρ_v and ρ_h. Measurements of ρ_h are shown in Figure 10. The fact that ρ_h is less than unity is evidence that the scattering units are large compared to the wave length of light and helps to explain the discrepancies with Gans' theory. For any one solvent, the smaller the values of ρ_h, the larger are the scattering units; hence Figure 10 shows that the scattering units become smaller at lower concentrations. This can be correlated with the form of the intensity curves (Figure 5) when it is realized that particles large compared to the wave length of light scatter less light as they become large. Depolarization factors for the benzene solutions are not given because the intensity for the solution was so low compared to that from the solvent that the values were influenced by the scattering from the pure solvent. A correction is difficult to apply because of the nonadditive character of the scattering (*22*).

In Krishnan's analysis, the size of the scattering unit is also indicated by $\Delta\rho_u = \rho_u - \frac{2\rho_v}{1+\rho_v}$. These values are plotted in Figure 11, and the data again show an increase in the size of the scattering unit with the concentration. The factor $2\rho_v/(1+\rho_v)$, which is the part of ρ_u because of the anisotropy of the scattering units, is plotted in Figure 12 and also increases with concentration. At zero concentration. the value agrees fairly well, for the ether solution, with

the depolarization predicted by Gans' theory for plate-shaped particles. The anisotropy factor is a large part of ρ_u, showing that the scattering units have a large anisotropy. Gans' theory predicts an increase of the depolarization with the concentration but, for these comparatively dilute solutions, the writers do not consider that the increases observed are due to this cause. The principal reasons for this view are the decrease of ρ_h with concentration and the fact that the depolarizations do not correspond to those provided for by the theory. As a check on the accuracy of the depolarization measurements, the measured values of ρ_v and ρ_h can be inserted in Equation 6 and values of ρ_u can be calculated to compare with the measured values. In general, a fair agreement is obtained. The equipment was also checked by comparing depolarizations measured for the pure solvents with those given in the International Critical Tables.

Some observations on the depolarization factors for more concentrated solutions are given in the following table; the rubber used for these solutions was 10 per cent by volume petroleum-ether diffusion rubber, but of a different batch from that used for previous data:

Solvent	ρ_h	ρ_v	ρ_u Obsvd.	ρ_u Calcd.	$\frac{2\rho_v}{1+\rho_v}$	$\Delta\rho_u$
Ethyl ether	0.418	0.0428	0.137	0.139	0.0821	0.0549
Heptane	0.353	0.0440	0.147	0.161	0.0844	0.0626
Benzene	0.445	0.0949	0.305	0.281	0.1731	0.1319

The depolarization factors, ρ_u, for these solutions are as large as those observed for pure liquids such as the solvents; but for these liquids $\rho_h = 1$, indicating that the cybotactic groups are small compared to the wave length of light, whereas the scattering units in the rubber solutions are large.

Use of Equation 7 makes possible a calculation of the length of the scattering unit, if the assumptions involved are accepted. Substituting $\rho_h = 0.535$ corresponding to the measurement of a 2 per cent solution in ether, and $\lambda' = 5800$ Å. $\times \frac{1}{1.35}$, l comes out as 5900 Å., in somewhat better than qualitative agreement with values given by Schulz (*30*) for the size of the colloidal unit from viscosity and osmosis measurements. For the ether solution at 0.1 per cent concentration, l is, by the same calculation, 3600 Å. Assuming the usual spacings and angles for the rubber hydrocarbon chain molecule, this would correspond to a molecular weight of 53,000. For the carbon tetrachloride solutions l is 7400 Å. at 2 per cent and 3400 Å. at 0.1 per cent. The curves decrease so rapidly that it is difficult to extrapolate them to zero concentration.

Conclusions

Analysis of the light scattered transversely by rubber solutions indicates that the units of structure responsible for the scattering are large compared to the wave length of

light and possess a high degree of anisotropy. The scattering in many respects resembles that from a pure liquid more than that from a colloidal suspension. This is especially true for solvents of refractive index nearly the same as that of rubber and for high concentrations. In view of these facts the most probable view in regard to the structure appears to be that it is a loose structure of anisotropic groups with hindered rotation analogous to the cybotactic groups in a liquid.

Acknowledgment

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The Absorption and Diffusion of Water in Rubber

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I. INTRODUCTION

The course of absorption or desorption of liquids by colloidal materials under various conditions is a subject of great scientific and technical importance, and there is already a mass of literature on the subject, for example, in connection with celluloid, leather, gelatin, and clays. The present paper deals only with the absorption of water by rubber; but it is anticipated that the results of this work may find some application or suggest lines of enquiry in other fields.

Most of the published work on the absorption of water by rubber is concerned with the amount absorbed under conditions of equilibrium with atmospheres of known humidity, or with solutions of known vapor pressure, and comparatively little with time relations before equilibrium is established or during fluctuating conditions. That this non-equilibrium period is often important may be shown by the following typical cases of practical interest.

(*a*) One of the costly major operations in the preparation of raw rubber on the plantation is the drying of the rubber after coagulation and washing. This process is limited by the rate of diffusion of moisture through the rubber, and any acceleration of the process would be of great economic importance to the industry.

(*b*) It is frequently necessary to investigate the amount of water which rubber will absorb under equilibrium conditions. As the time taken to reach equilibrium under ordinary test conditions may be many months, it is important to decide to what extent the final absorption can be predicted from short period tests.

(*c*) In electric cables, especially submarine cables where the dielectric is able to take up water from the sea, the various electrical properties which affect the transmission properties are differently affected by the spatial distribution of the absorbed moisture through the dielectric. Similar problems occur with solid insulators in which the surface resistivity and other electrical properties are differently affected by periodic changes of ambient humidity.

The study of these aspects of the subject requires the establishment of a satisfactory differential equation of diffusion of moisture through the rubber, and it has previously been assumed that a simple equation which applies to the diffusion of gases applies equally well to the case of water. It is the purpose of this paper to show that the simple equation does not apply, to substitute a modified equation which agrees more nearly with observations, and to draw attention to important consequences of this departure from the simpler diffusion laws.

II. THEORY OF TIME-ABSORPTION CURVE

1. Simple Gases in Rubber

(*a*) *General Laws of Diffusion.*—In order to make clear the special behavior of water, it is recalled that simple gases obey Fick's and Henry's laws, the appropriate differential equation for the case where concentration varies in one dimension only being:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (1)$$

where c is the concentration at time t in a plane at a distance x from the origin measured in the direction of diffusion, and D is the diffusion constant. This is analogous to the case of conduction of heat.

(*b*) *Diffusion in an Infinite Sheet.*—The case of most frequent interest for experimental purposes is that of a sheet of thickness $2a$, and of such extent that edge

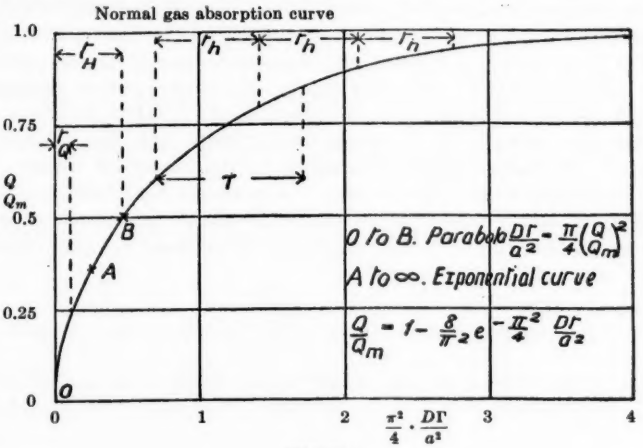
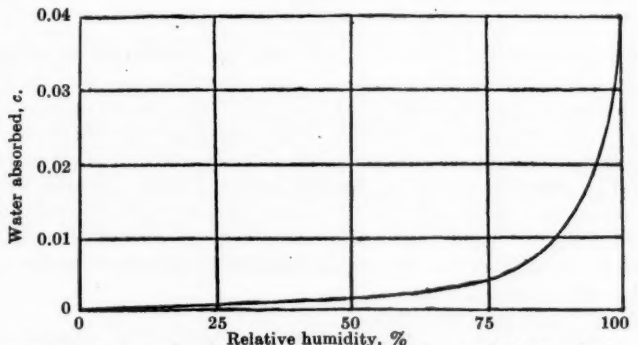


Figure 1



Relation between humidity and absorbed water in a typical vulcanized rubber.

Figure 2

effects may be neglected, initially free from the gas, but suddenly immersed at time $t = 0$ into gas maintained at a fixed partial pressure.

In diffusion experiments it is usual to measure the total quantity absorbed, and solutions for this case are given by Andrews and Johnston,[1] and McKay.[2] Their principal conclusions for our purpose may be expressed thus:

(i) If Q and Q_m are the quantities of gas absorbed at times t and ∞, respectively, the degree of saturation as shown by Q/Q_m may be expressed as a series in terms of a single parameter $\tau = 4a^2/\pi^2 D$ which may be called the *time constant*.

(ii) The curve connecting Q/Q_m with τ, which will be called the *normal gas*

absorption curve, is shown in Fig. 1, and can be closely represented over the whole range by a combination of two approximations as shown in the figure.

2. Diffusion of Water Vapor in Rubber

In previous literature on the subject[3] it has been assumed that diffusion of water through rubber can be expressed by the differential equation (1) applicable to gases; but in view of the complex nature of the absorption of water by rubber[4] it is desirable to examine this assumption more critically.

Since the absorption is largely due to the formation of a solution of water-soluble substances within the rubber, it is to be expected that the rate of diffusion at any point will be proportional to the gradient of osmotic pressure instead of the gradient of concentration of water. In other words, the symbol c now represents quite different properties on the two sides of the equation (1). On the left it represents the concentration of water in the rubber, while on the right it is a function of the concentration of water-soluble substances in the absorbed water. Now the difference between the osmotic pressures of two aqueous solutions is proportional to the difference between the relative humidities (R. H.) of the atmospheres which would be in equilibrium with the solutions. Equation (1) must, therefore, be rewritten:

$$\frac{\partial c}{\partial t} = D^1 \frac{\partial^2 h}{\partial x^2} \tag{2}$$

where

h = relative humidity of the atmosphere, which would be in equilibrium with the internal solution at x (to be called the "equivalent humidity"),

and

D^1 = a constant depending on the rubber. (The possibility of its varying with the amount of water absorbed must be borne in mind.)

Moreover, the relation between c and h can be determined experimentally by measuring the equilibrium absorption of water by rubber in solutions or in atmospheres of known relative humidity,[5] and is of the type shown in Fig. 2, the shape of the curve depending on the rubber. The vulcanized sample shown was made from commercial smoked sheet, and contained 5 per cent combined sulfur.[4]

It should be noted that c in Fig. 2 is the weight of water per unit weight of dry rubber, whereas in equation (2) it is the volume of water per unit volume of rubber plus absorbed water. As the amount of water is usually small, this difference may be left out of account for the present in considering the shape of the relative humidity/absorption curve.

Equation (2) may now be written

$$\frac{\partial h}{\partial t} \cdot \frac{\partial c}{\partial h} = D^1 \frac{\partial^2 h}{\partial x^2} \tag{3}$$

This is the equation which is proposed to replace the commonly accepted equation (1). The consequences of the revised theory and the evidence of its validity are considered below.

III. STUDY OF TIME-WATER CONTENT CURVE IN LIGHT OF REVISED THEORY

Since $\partial c/\partial h$ is not constant (see Fig. 2), the solutions of equation (1) cannot now be used either to determine c or h as a function of x and t, or to obtain the total absorption at a time t by integrating c with respect to x. However, pending a solution to equation (3), some useful conclusions may be drawn which may be made

the basis of experimental tests of the theory. It is proposed to consider several aspects of the problem, (*a*) to indicate in what way water diffusion is expected to differ from gas diffusion, (*b*) to cite published work bearing on these predictions, and (*c*) where published information is lacking, to describe new experiments.

In this connection, it is pointed out that the theory applies only to conditions in which equilibrium can be reached. Consequently, it is necessary to leave out of consideration most of the published work on the drying of raw rubber, where the initial and final states are usually indefinite, on the drying of freshly coagulated rubber, which appears to be a very complicated system, and on the absorption of water by unvulcanized rubber at very high humidities, where equilibrium is seldom reached.

1. Time-Absorption Curve with Narrow Range of Humidity

(*a*) If a sheet saturated at relative humidity h_1 is transferred to another humidity h_2, so close to h_1 that $\partial c/\partial h$ may be considered constant from h_1 to h_2, the time-absorption relation is similar in form to the solution of equation (1) writing $D^1/\frac{\partial c}{\partial h}$ for D and $\frac{Q-Q_i}{Q_m-Q_i}$ for Q/Q_m, where Q_i = quantity of water uniformly absorbed initially. The expression $4a^2\frac{\partial c}{\partial h}/\pi^2 D^1$ now takes the place of $\frac{4a^2}{\pi^2 D}$ as the time constant of the curve. Since $\partial c/\partial h$ increases with humidity and also, usually, with the hydroscopicity of the rubber, the time taken to reach a given value of $\frac{Q-Q_i}{Q_m-Q_i}$ will increase with these factors also, whereas if the simple gas diffusion equation (1) applied, the time constant would be independent of them.

(*b*) Confirmation of this prediction has been found with finely rasped samples of unvulcanized and vulcanized rubber[6] and with gutta-percha and Paragutta, a submarine cable insulating material consisting of deresinated balata, deproteinized rubber, and wax.[7]

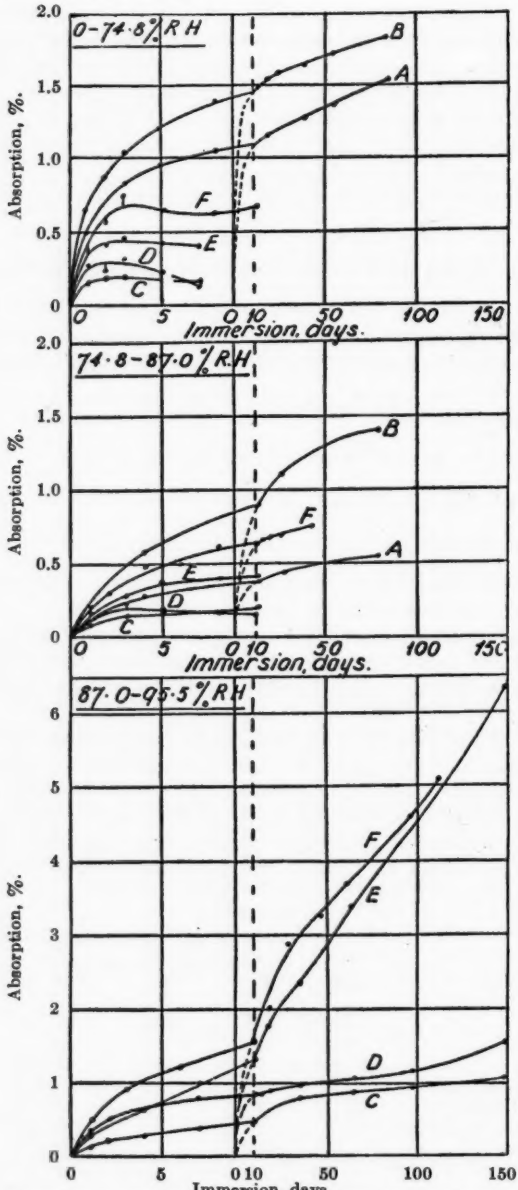
(*c*) In most of the experimental work to be described in this paper, rubbers of known composition which had been made up in the laboratory for other purposes were used. They were selected to cover a wide range of behavior in regard to water absorption rather than to isolate the effects of the components of natural rubber, or to exhibit the influence of particular ingredients or conditions of vulcanization. The ingredients are shown in Table I. All the samples were vulcanized normally

TABLE I

	Rubber Sample					
	A	B	C	D	E	F
Smoked sheet rubber	100	100	100	100	100	...
Para rubber	...	...	...	...	...	100
Zinc oxide	62	62	50	65.5	...	...
Gas black	30	30	1.5	...	...	...
Sulfur	6	7.2	3	2.5	5.3	5.3
Triphenylguanidine	2	2.4	...	...	...	...
Mercaptobenzothiazole	...	...	0.7	...	...	...
Tetraethylthiuram disulfide	..	...	...	0.5	...	...
Alkali tire reclaim	...	40	...	...	...	...
Paraffin wax	...	...	3.5	...	...	...
French chalk	...	...	40	...	...	...

(*i. e.*, nearly to maximum tensile strength), except those from mixings having a high percentage of sulfur, in which cases samples which did not exhibit "blooming" of sulfur to the surface were chosen to avoid complications due to loss of free sulfur

in handling. Since this involved over-vulcanization, the aging properties of the rubber in those cases were inferior.



Absorption curves for rubber strips in saturated salt solutions.

Figures 3, 4, and 5

To minimize the thickness in one dimension, most of the specimens used were parts of the outer rings from which Schopper tensile test rings had been punched,

the dimensions being: internal diameter, 52.3 mm.; axial thickness, about 5 mm.; radial thickness, 2.3 mm. One specimen, D, however, was a disc 0.73 mm. thick and 44 mm. in diameter.

After preliminary drying *in vacuo* for 4 days at 70° C., the specimens were immersed in an appropriate salt solution in stoppered bottles, and maintained at 34° C. At intervals the specimens were withdrawn, superficially dried, weighed in tared, stoppered bottles, and reimmersed. The solutions were kept saturated by the presence of an excess of the salt. The salts used, and their equivalent humidities at 34° C. were as follows:[8] sodium chloride, 78.4% R. H.; sodium sulfate, 87.0% R. H.; potassium sulfate, 96.5% R. H. After the preliminary drying each specimen was placed in the sodium chloride solution and weighed at intervals until equilibrium was reached, then transferred to the next solution in order of humidity, and so on. In some cases the whole series was not completed, since equilibrium was not reached in a reasonable time.

The absorption, in excess of the final absorption at the previous humidity, expressed as a percentage of the dry weight is shown in Figs. 3, 4, and 5.* In some cases the absorption was so small that the half-saturation period t_H could not be determined accurately. The immersion of A and B had to be longer than that of the other specimens, and, as it was thought that the failure to reach equilibrium might be due to oxidation, the specimens were transferred to the second solution without waiting for equilibrium; they were not immersed in the third solution. Specimen D behaved in a peculiar way, the absorption in the solutions of lower humidity rising to a maximum and then decreasing, as if soluble material were being extracted; this is not uncommon with certain rubbers. Specimens E and F, which were expected to have bad aging properties, did not reach equilibrium at the highest humidity.

In spite of the errors inherent in these small measurements, it is evident that, with any of the rubbers tested, the half-saturation period increases rapidly with the mean humidity over which the absorption takes place, as predicted by the osmotic theory. Further, there is a rough but quite distinct parallelism between the hygroscopicity of the rubber and the half-saturation period. (In this comparison sample D must be excluded, since it differed in dimensions from the others.)

2. Time-Absorption Curve over Wide Range of Humidity

(*a*) Although the time-absorption curve for a rubber changing from equilibrium at one humidity to equilibrium at a much higher humidity cannot be calculated without the complete solution of equation (3), the following considerations will throw some light on the general shape of the curve. The concentration of water, and therefore the value of $\partial c/\partial h$, at each point in the rubber increases continuously with time. For each increment in equivalent humidity, both the capacity of the rubber to absorb water, and the time constant of the time/equivalent humidity curve increase rapidly. These effects may be represented in a general way as a modification of the normal gas absorption curve by continuously expanding absorption and time scales. These effects would be more marked the higher the hygroscopicity of the rubber, and the higher the humidity of exposure.

The effect of variation in $\partial c/\partial h$ may be represented by a similar variation of specific heat in the analogous case of thermal conduction. If a sheet of metal, for example, at a uniform temperature of 0° C. were immersed in boiling water and the specific heat of the metal increased rapidly between 75° and 100° C.,

* In this, and also Figs. 6, 8, 9, and 10, two time scales are used, the earlier part of each curve being plotted on an open scale and the latter part on a closed scale, with the earlier part shown dotted to indicate the shape of the complete curve.

the heat absorption would follow the same course as water absorption by a rubber sheet. In the later stages, not only would the quantity of heat involved in changing the average temperature by a given amount be greater, but also the approach of each volume element to its final temperature would become slower.

(*b*) Andrews and Johnston[1] have shown that when sheets of a given rubber of various thicknesses are immersed in water, and the amount of water absorbed, expressed as a fraction of the saturation value, is plotted against time/(thickness)$_1^2$ all the points lie on a single curve; but this curve differs in shape from that predicted from equation (1), the initial rate of rise being relatively too great. The difference in shape was attributed by the authors to variation in structure through the sheets due to calendering, but it now appears that equation (3) is sufficient to explain both the variation of rate of absorption with thickness (section (3)), and the then unexpected shape of the time-absorption curve.

Confirmation of the above theory for cases in which equilibrium has been reached at lower humidities is found in the work of Fry,[9] and of Messenger and Scott,[10] both using crepe rubber, and of Kemp,[7] using gutta-percha and Paragutta.

A few confirmatory observations are available to show the variation of time-absorption curve with hygroscopicity of the rubber. These are in the work of Lowry and Kohman,[4] who examined portions of a sample of commercial smoked sheet washed for various periods, and of Boggs and Blake[11] working with chemically purified rubber hydrocarbon.

(*c*) The shape of the time-absorption curve over a wide range of humidity is shown by the following experiments.

In order to obtain equilibrium in a short time, and so reduce the risk of oxidation effects, very thin sheets, both of substantially unloaded vulcanized rubber, were used, and a final humidity of 96.5% R. H. was adopted instead of 100%. The available materials were (*a*) golf ball tape about 0.16 mm. thick, and (*b*) sheet made from vulcanized latex about 0.13 mm. thick, which would contain more of the water-soluble components of the natural rubber than (*a*).

After preliminary drying, the specimens were immersed in saturated solutions of potassium sulfate at 34° C., and were taken out at intervals, superficially dried, and weighed in tared, stoppered bottles. Similar samples, which had been soaked in the solution for 11 days at 34° C., were dried in a desiccator at 34° C., and weighed at intervals until constant in weight.

The absorption and desorption curves are shown in Fig. 6. It will be seen that in both cases, on drying, the weight falls to a little below its original value before immersion. If, as seems probable, this is due to extraction of water-soluble substances, it may be assumed that the latter part of the absorption curve has been somewhat flattened thereby.

The analysis of the absorption curves is shown in Table II.

TABLE II

Portion of Curve	Time Occupied, Hours	
	Tape	Vulcanized Latex Sheet
0 to $^1/_2$-saturation (t_H)	0.5	2.0
$^1/_2$ to $^3/_4$-saturation (t_h)	2.7	15
$^3/_4$ to $^7/_8$-saturation (t_h)	3.8	55

The following results, which are in accordance with the osmotic theory, will be noted from the table:

(I) The shape of the time-absorption curve differs from that of the normal gas-absorption curve in the manner predicted.

The half-value-period t_h in lines 2 and 3 is much greater than the value of $1.43t_H$ appropriate to a simple gas, and increases with time.

(II) The departure from the form of the normal gas-absorption curve is more marked with one rubber (vulcanized latex) than the other; the curves cannot be superposed merely by an adjustment of the time scale of one curve. This would be expected if the shapes of the humidity/absorption curves differed.

Similar effects were shown in absorption and desorption curves with a specimen of rubber C, as described in Section III (1). The technic was similar except that

Absorption and desorption curves for thin sheets in a saturated salt solution (96.5% R. H.)

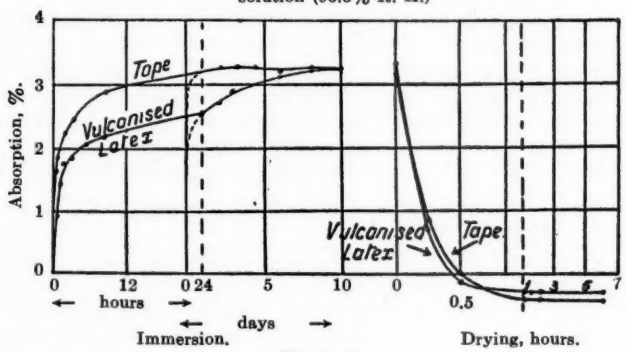


Figure 6

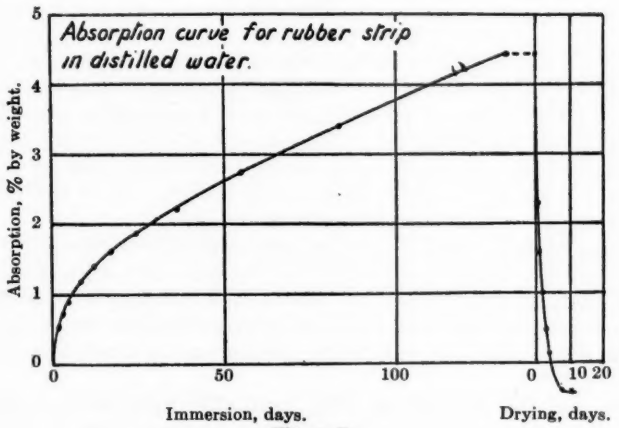


Figure 7

the liquid was distilled water, which was renewed frequently to avoid contamination. The results are shown in Fig. 7.

3. Variation of Saturation or Drying-Period with Thickness

(*a*) The theory of Andrews and Johnston[1] that the time taken to reach a given stage of saturation varies as the square of the thickness of the sheet can easily be shown to be consistent with the new equation (3), as well as the old equation (1).

(*b*) The experimental results of Andrews and Johnston are, therefore, consistent with the new theory, as also are those of Boggs and Blake,[11] who found that,

with sheets of different thickness of one rubber, the early portions of the time-absorption curves coincided when absorption was expressed in terms of gain in weight per unit surface area. This result follows from either theory if the time-absorption curves are parabolic, as is the case with the curves in question within the accuracy of measurement of the printed curves.

Van Harpen[3] has shown that the time of drying of raw rubber varies as the square of the thickness of the sheet.

4. Drying Curve

(*a*) According to equation (1), the time curve for a gas diffusing into a sheet is simply the inverse of that for a gas diffusing out. This is not the case for water vapor behaving in accordance with equation (3), and some important conclusions may be drawn as follows:

Shape of Curve.—One would expect the shape of the desorption (or drying) curve to differ from that of the absorption (or soaking) curve in that the approach to the asymptote would not be so slow in the former case, especially in the later stages of the process. The time constant $4a^2 \frac{\partial c}{\partial h}/\pi D^1$ should now decrease with time instead of increasing, causing the final approach to the end-point of the drying process to be much quicker.

Time Required for Drying.—The time required for the loss of a given amount of water from saturated rubber should be very much less than that required for the absorption of the same amount by dry rubber. Refer again to Fig. 2 and consider the differences of equivalent humidity between some point well inside the rubber, and another just within the boundary, which may be assumed either dry or saturated as the case may be. In absorption, it is seen that by the time half-saturation (2 per cent absorption) is reached at the point inside the rubber, the equivalent humidity difference between the two points has fallen to 4.5 per cent of its original value, whereas after desorption to the same state it is still 95.5 per cent of its original value. After absorption to 0.9 saturation, and drying to 0.1 saturation, the equivalent humidity differences are about 0.5 per cent and 72.5 per cent, respectively. The bulk of the water is therefore absorbed under the influence of a low osmotic pressure difference in soaking, and is lost under the influence of a high osmotic pressure difference in drying.

Similarity of Absorption and Desorption Curves over a Narrow Range of Humidity.—Effects (I) and (II) noted above arise from the great curvature of the humidity-absorption relationship of rubber. If, the humidity changes were confined within narrow limits so that $\partial c/\partial h$ remained constant over the whole range, the differences between the shapes and time scales of the absorption and desorption curves should disappear.

(*b*) *Time Required for Drying.*—The great difference between the times required for absorption and desorption is shown by the results of Fry[9] with raw rubber, and of Cooper and Scott[12] with cold-cured rubbers.

This more rapid drying or desorption over a given range of humidity must not be confused with the slower desorption observed by Kemp (Section III (1)), in which the absorption and desorption took place over mutually exclusive ranges of humidity.

Bradley, McKay, and Worswick,[13] in a very similar investigation on diffusion of water vapor in leather, found that between 0 and 30 per cent R. H. the time for drying was much greater than for "wetting," the reverse of the effect observed with rubber; but the curvature of the humidity-absorption graph also was opposite in direction to that of rubber over the range concerned.

(*c*) *Comparison of Absorption and Desorption Curves.*—The relative shapes and time scales of the absorption and desorption curves are shown in the experiments described in Section III (2) (Figs. 6 and 7). There the drying was so rapid that it is not possible to analyze the curves accurately, but it will be seen that in drying there was no very slow approach to the final value as in absorption, and that both samples were dry within a very short time compared with that required for saturation.

The main object of the next experiment was to study the relative rates of attainment of equilibrium in absorption and desorption over various restricted ranges of humidity under conditions of rapid attainment of equilibrium, and, therefore, less risk of interference by oxidation. In particular, it was intended to obtain confirmation of the prediction from the osmotic theory that over a humidity range so small that the humidity-absorption relationship could be considered linear, the half-saturation and half-drying periods would be equal. Unfortunately, accurate determinations under such conditions are extremely difficult, and the experiments were therefore confined to demonstrating a simpler case of the same problem, *viz.*, that if a given humidity range is divided into two smaller ranges, so that the humidity-absorption relationship is more nearly linear in each small range than over the whole range, then in each small range the half-saturation and half-drying periods will be more nearly equal than those for the whole range. It was intended, also, to compare the shapes of the absorption and desorption curves, although the actual shape in either case could not be predicted, owing to the irregularity of size and form of the finely divided rubber.

The rubbers used for these tests were B and E, as described in Section III (1). They were finely divided by rasping, spread on watch-glasses, as is usual in the R. A. B. R. M. method of determination of water absorption (Daynes),[5] and exposed at 20° C. to atmospheres of one humidity, weighings being taken at short intervals up to equilibrium. The watch-glasses were then transferred to jars containing atmospheres at other humidities as required, and the process repeated. Each of the two rubbers was subjected in this way to the following cycles of exposure:

(*a*) 0 per cent R. H.–86.8 per cent R. H. (sodium sulfate)–0 per cent R. H.

(*b*) 0 per cent R. H.–75.0 per cent R. H. (sodium chloride)–86.8 per cent R. H.–75.0 per cent R. H.–0 per cent R. H.

The absorption and desorption curves are shown in Figs. 8, 9, and 10.

The values of t_H under various conditions are shown in Table III, together with the ratio of t_H for rising and for falling humidities.

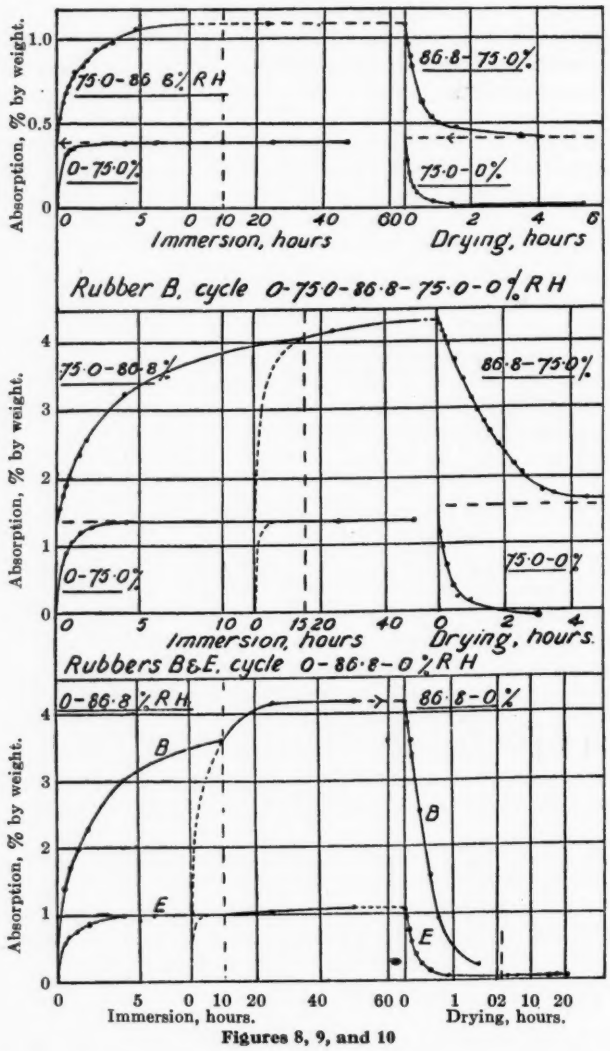
TABLE III

Rubber	Humidity Range Per Cent R. H.	t_H in Min. for Rising Humidity (H. S. P.)	t_H in Min. for Falling Humidity (H. D. P.)	Ratio H. S. P./ H. D. P.
B	0–86.8	84	24	3.5
	0–75.0	18	15	1.2
	75.0–86.8	160	73	2.2
E	0–86.8	27	9	3.0
	0–75.0	<10	6	<1.7
	75.0–86.8	42	18	2.3

It is seen that the osmotic theory is confirmed in that: (*a*) the ratio half-saturation period (H. S. P.)/half-drying period (H. D. P.) for the smaller ranges of humidity 0–75.0 per cent and 75.0–86.8 per cent is greater than unity, but is nearer unity than for the whole range 0–86.8 per cent, and very much less than that

observed in previous experiments (Figs. 6 and 7), with still larger ranges of 0–100 per cent and 0–96.5 per cent; (*b*) the higher the hygroscopicity of the rubber, and the higher the mean humidity of the atmosphere during the change, the greater is the value of t_H.

Absorption and desorption curves for rasped rubbers in atmospheres of various humidities.
Rubber E, cycle 0–75.0–86.8–75.0–0% R. H.



Figures 8, 9, and 10

In Figs. 8, 9, and 10 the difference in shape between absorption and desorption curves is very noticeable where there is a wide change of humidity. The drying curve is comparatively straight at first, and sharply curved at the end. The reverse is found in the absorption curve. This difference is not so clear in the

more restricted changes of humidity, particularly over the range 0–75 per cent R. H., where $\partial c/\partial h$ is known to be nearly constant.

IV. CONCLUSIONS

We may now summarize the main results of the investigation.

(1) Predictions based on the differential equation (3) are substantially confirmed by the results of various workers, and the simpler gas diffusion equation (1), which is usually assumed, is shown to be inapplicable to the case of water vapor in rubber. The confirmation being somewhat indirect, it would be desirable to obtain more direct evidence by measuring the rate of diffusion of water vapor through thin rubber films under equilibrium conditions with various small differences of humidity between the two sides of the film. In that way it would be possible to obtain more precise information as to the relation between rate of diffusion and osmotic pressure gradient, and thus as to the extent to which the "diffusion constant" D^1 is independent of the water-vapor concentration.

(2) When a sample of rubber changes from equilibrium at one humidity to equilibrium at a much higher humidity, the time-absorption curve is characterized by a rapid initial rise, and an approach to equilibrium that is much more prolonged than if the simple gas-diffusion equation applied. The higher the humidity being approached, and, generally, the greater the hygroscopicity of the rubber, the more marked is this slowness of approach to equilibrium, and the greater is the time required for, say, half the total change in water content to occur.

(3) When a sample of rubber changes from equilibrium at one humidity to equilibrium at a neighboring humidity, the time required for, say, half the change in water content increases with the mean humidity, and, generally, with the hygroscopicity of the rubber.

(4) When desorption takes place in a sample of rubber changing from equilibrium at one humidity to equilibrium at a considerably lower humidity:

(*a*) the early part of the time/water content curve is comparatively straight, and the approach to equilibrium fairly abrupt;

(*b*) the time required for, say, half the change in water content to occur is much less than the corresponding time in the process of absorption between the same humidity limits;

(*c*) the smaller the range of humidity over which the change occurs, the more nearly is the curve similar in shape and time scale to that which would occur with a rising humidity over the same range.

(5) When rubber sheets which are identical except in thickness are subjected to changes in ambient humidity, the time required for, say, half the change in water content to occur varies as the square of the thickness. In this respect there is no difference between the predictions of the old and new diffusion equations.

More generally, we may say that the time relations in absorption and desorption of water vapor in rubber are determined very largely by the shape of the humidity-absorption curve for the particular rubber under consideration, and that the further study of such relations in connection with practical problems demands a solution of the new differential equation.

V. SUMMARY

A new differential equation of diffusion is put forward to represent the movements of water vapor through rubber in accordance with the osmotic theory of absorption.

Experiments are described which, together with the evidence quoted from

existing knowledge, confirm a number of predictions as to differences between the absorption of a gas and of water vapor by rubber. These predictions deal with the shapes of the absorption- and desorption-time curves between narrow and wide limits of humidity, the relative times required for absorption and desorption, and the variation of absorption and desorption periods with thickness of the rubber sheet. The results are definitely inconsistent with the simple gas-diffusion theory, which is often assumed to apply to water in rubber. It is established that the shape of the humidity-absorption curve is a dominant factor in determining time-water content relations. Except for changes over very restricted ranges of humidity, the absorption- and desorption-time curves are of different shape, and desorption is much more rapid than absorption. The periods required for absorption and desorption are greater, the higher the humidity and the higher the hygroscopicity of the rubber. The law that the time required to reach a given stage of saturation varies as the square of the linear dimensions of the sample (the shape being constant) is equally true for diffusion, according to the old and new equations.

Future progress in the application of the osmotic theory to a number of practical problems, some of which are indicated, will depend largely on the solution of a differential equation of the type:

$$\frac{\partial h}{\partial t} = D^1 f(h) \frac{\partial^2 h}{\partial x^2}$$

in which the form of the function $f(h)$ varies with the water-absorbing components of the rubber.

Acknowledgment is made of the kindness of the Board of Management of the Rubber Research Association in permitting the publication of this investigation, which was communicated to their members, as *Laboratory Circulars*, Nos. 98 and 108, June, 1932, and February, 1933.

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Nature of the Diffusion Process in Rubber

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It is known[1] that silica-gas diffusion systems exemplify a type of non-specific activated diffusion process, as opposed to the specific type of diffusion system, such as hydrogen-palladium. It seemed that the diffusion of gases through other "glass-like" materials such as some organic membranes, for example rubber, might offer further examples of non-specific activated diffusion. The data needed to test this hypothesis were available in papers by Edwards and Pickering,[2] and by Dewar.[3] Graham[4] first noted the large temperature coefficient of the diffusion process through rubber, and that the diffusion velocities had no connection with the molecular weights.

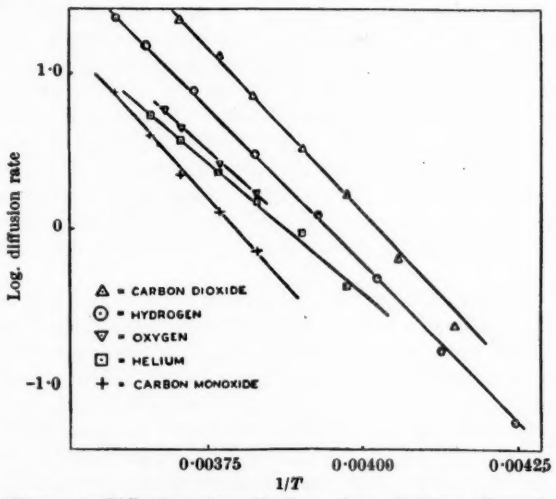

Figure 1—Diffusion through Pure Para Rubber (Dewar's Data). Diffusion Rate in cc. per day per sq. cm. per atm.; Thickness of Membrane, Approximately 1 mm.; T = Absolute Temperature

Edwards and Pickering's data for the diffusion of hydrogen, helium, and carbon dioxide through vulcanized rubber, and Taylor, Hermann, and Kemp's data[5] for the diffusion of water through vulcanized rubber, give good straight lines when log (diffusion rate) is plotted against the reciprocal of the absolute temperature (T), with the exception of the data for carbon dioxide at temperatures of 80° and 100° C. Similarly Dewar's data (Fig. 1) for diffusion of hydrogen, helium, carbon monoxide, carbon dioxide, and oxygen through pure para rubber give linear log (diffusion rate) *vs.* $1/T$ curves. Energies of activation calculated from these curves for vulcanized and for para rubber are given in the accompanying table. They are very much larger for pure para rubber than for vulcanized rubber.

Vulcanized Rubber			Para Rubber		
Gas	Energy (Cal./Mol.)	Author	Gas	Energy (Cal./Mol.)	Author
He	6300	Edwards and Pickering	He	15,400	Dewar
H_2	6470	Edwards and Pickering	H_2	19,000	Dewar
	5900	Daynes[6]			
CO_2	7580	Edwards and Pickering	CO_2	19,100	Dewar
H_2O	2780	Taylor, Hermann, and Kemp			
			O_2	16,300	Dewar
			CO	19,000	Dewar

The solubility of these gases in rubber varies only slightly with temperature,[7] so that no explanation save one involving activated diffusion can account for the velocity *increasing* exponentially with temperature.

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The Viscosity of Latex and of Latex Mixtures

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For the rubber technologist, a change in the plasticity of rubber mixtures is one of the most important indications that fundamental changes are taking place within the mixture. For example, a decrease in plasticity would lead to the conclusion that incipient vulcanization had taken place, and an increase in plasticity would indicate degradation resulting from unfavorable conditions of storage, from the action of deleterious substances in the rubber, etc. Corresponding to these increases and decreases in plasticity in the case of dry rubber mixtures, increases or decreases in the viscosity of rubber solutions are found. These changes in viscosity and plasticity unquestionably conform to the facts which are now known about rubber and its behavior on degradation and on vulcanization. Further, latex, which is becoming of increasing importance, and mixtures prepared from it, undergo changes in viscosity on standing as well as during the processes of manufacture. There are many of these changes in the viscosity of latex, and accordingly it is much more difficult to ascertain them individually than it is in the case of solutions in organic solvents. It might be of importance to know more about the factors which influence the viscosity of latex. Then again in studying the viscosity of latex a great number of phenomena and problems are encountered which require explanation, so that a report of all the observations made during our investigation may be found of general interest.

Viscosity, or internal friction, represents a force, or rather that force, which is necessary to displace the particles with respect to one another. The value of the absolute viscosity expressed in "poises" indicates what force in dynes is necessary to move the upper surface opposite and parallel to the lower surface at a rate of 1 centimeter per second in a liquid of 1 cubic centimeter area and 1 centimeter depth. In many cases the absolute viscosity is not determined, but only the relative viscosity, *i. e.*, by determining how many more times viscous the substance is than the control. To measure the internal friction there are in principle three different methods and, correspondingly, three different types of apparatus.

(1) Flow, or capillary, viscometers.
(2) Falling ball viscometers.
(3) Rotation viscometers.

Capillary viscometers are not particularly well adapted to the determination of the viscosity of latex, first, because latex is an opaque liquid and therefore the surface of the liquid cannot be observed well; secondly, because the surfaces are exposed and films are readily formed, especially in concentrated latices; and thirdly, because it is difficult to clean out the latex from the capillaries. Since in general the viscosity values for latex are relatively low, the falling ball method is likewise only of limited application because turbulence occurs at low viscosities.

On the contrary, a viscometer which has recently been developed appears to be

well adapted as a measuring instrument for latex. This instrument is the Höppler viscometer, in which the capillary method is combined to a certain extent with the falling ball method. In this viscometer the ball does not fall freely through the liquid, but it forces the liquid through a narrow crescent-shaped constant gap between the ball and the wall of the tube. The ball in the Höppler viscometer can be clearly observed in the opaque latex; the liquid is completely shut off from air, no drying can take place, and therefore it is easy to clean this viscometer of latex. In the present work the absolute viscosity of latex was determined with this instrument. The author had had no experience with the rotation viscometer which, in the form of the torsion viscometer of Couette, is theoretically the best instrument. In "Latex in Industry" Noble[1] published determinations of the absolute viscosity of latex at various concentrations, which were carried out by means of the Stormer rotation viscometer.

For determining the relative viscosity of latex and latex mixtures in an approximate way, the falling ball viscometer having a light, small glass bulb with a glass stem (see Fig. 1) was found to be of service. This stem had two marks 20 millimeters apart. The viscometer was allowed to sink through the liquid for this distance, and the time necessary to cover this distance was recorded. This viscometer

Figure 1

can be used satisfactorily only with slightly viscous mixtures. It is excellently adapted for following in a simple way, over a long period of time, viscosity changes of considerable magnitude, and in a long series of experiments. Experiments with this viscometer are so simplified that measurements of a mixture can be carried out in the container in which the mixture has been stored.

According to Einstein, the viscosity of a heterogeneous system like latex depends on two factors: (1) the viscosity of the dispersing agent, and (2) the space taken up by the dispersed phase. The mathematical formulation of the viscosity law is, according to Einstein:

$$\eta = \eta_0(1 + 2.5\, v/V)$$

This formula is valid only with certain assumptions, above all only for small values of v/V, *i. e.*, only at low concentrations. Viscosity measurements of latex with the Höppler viscometer likewise gave correspondingly higher viscosity values for concentrated latex, and a more rapid rise of the viscosity curve with the concentration than was to be expected from the viscosity law (see Fig. 2).

The latices of various concentrations required for these measurements were prepared from a 60 per cent latex which had been stabilized with ammonia and concentrated by centrifuging. The type of agent used for dilution, whether water or 1 per cent ammonia, was without influence on the viscosity values of diluted latices. Greater differences were found among various shipments of latex from the same supplier. For the 60 per cent concentrate, a maximum value of 0.65 and a minimum value of 0.45 were found. Corresponding viscosity values were found for

latices of lower concentration obtained by dilution. The curve shown in Fig. 2 corresponds to a latex of medium viscosity such as was used in most of the tests.

The values of latex of different concentrations obtained with the Höppler viscometer were, however, higher, in some cases very much higher, than the earlier viscosity values of other authors. The curves show the absolute viscosity of latex, determined by Cotton,[2] Bary,[3] Noble,[4] and Ditmar.[5] Cotton, Ditmar, and Bary give only the experimental values in seconds in comparison with the value for water. From these experimental data, the absolute viscosity was calculated in a rough way without correction, in part by interpolation. The corrections, in so far as they relate to the physical properties of latex, *e. g.*, density and surface tension, were small in relation to the deviations among the individual viscosity curves. Neither can the great differences be attributed to a difference in the original sub-

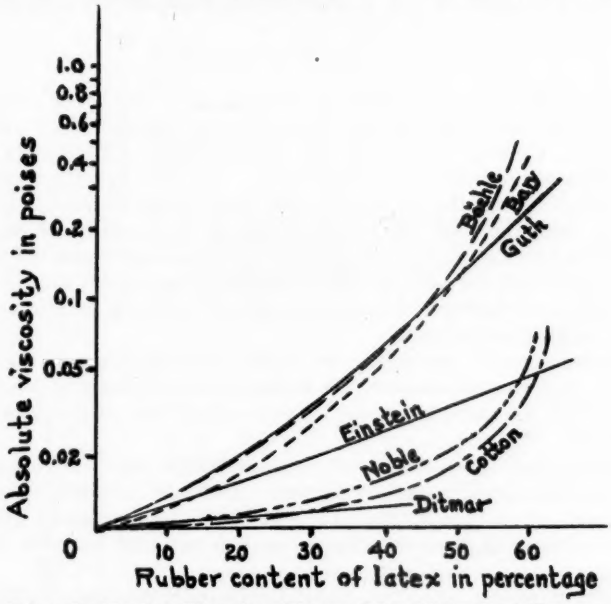

Figure 2—Absolute Viscosity of Latex of 0 to 60 Per Cent Concentration at 19–21° C., Based on the Results of Various Investigators and Calculated by the Viscosity Formulas of Einstein and Guth

stance tested by the various experimentors, for in that case, our measurements, which were carried out with a specially pure latex, would have given in all likelihood very small viscosity values. An examination of the experiments shows that only the method of measurement and the specific characteristics of the viscometer used can be held responsible for the varying results of viscosity determinations. In determining the viscosity by the suspended bulb method, two factors other than the Reynolds number, which is derived from the size of the apparatus and density of the substance, must be taken into account: first, the magnitude of the Reynolds number which is obtained from the diameter of the particles, and, secondly, the ratio of the width of the gap or cross-section of the capillary to the diameter of the particle. These important factors were not taken into account in the measurements, and the experimental technic is not described in sufficient detail for one to be able to make the corrections later. If the authors have neglected

to this extent to recalculate their experimental measurements in terms of the absolute viscosities and have been satisfied with experimental values in seconds, they have certainly not exercised critical foresight, in fact quite the opposite. Besides not taking these factors into account, measurements by the Höppler viscometer might be open to the further objection that the peculiarity of this apparatus, *viz.*, the crescent-shaped sharply projecting outflow, leads to false results, perhaps because the ball may be blocked irregularly in its path through the tube by latex particles which have reached a considerable size. The following points in support of the accuracy of measurements by the Höppler viscometer should, however, be considered.

(1) On the basis of theoretical heat and hydrodynamic considerations, analogous to Einstein's derivation, Guth[6] has recently developed a formula for the viscosity of suspensions of spheres at high concentrations which differs from the Einstein formula in only one quadratic factor:

$$\eta = \eta_0[1 + 2.5\ v/V + 7.8\ (v/V)^2]$$

The expression within the parenthesis is only the first member in a series of increasing powers, of which progressively more members must be added with increase in concentration. Up to now, however, only the coefficients of the first two numbers have been calculated. If the viscosity of latex is calculated by the Guth formula, with the assumption that the viscosity of the serum is approximately the same as that of water, then the theoretical values agree perfectly with the experimental values determined by the Höppler viscometer up to a rubber content of 45 per cent (see Fig. 2). Above 45 per cent of rubber, no further agreement is to be expected, because from this point on the higher powers of v/V lead to indefinite values when there are no limiting coefficients.

(2) A blocking would necessarily be evident by variations in the results of experiments. However, experiments show that whenever viscosity determinations are repeated with the same latex, the same times of flow within 1 per cent are always obtained.

(3) Blocking would also mean that the temperature and the viscosity of the latex would not be related in any simple way. However, viscosity measurements of 35 and 60 per cent latices between 15° and 70° C. by means of a Höppler viscometer gave the usual viscosity changes of 2–3 per cent for each degree (see Fig. 3).

(4) Finally, in favor of measurements in the Höppler viscometer is the fact that these measurements agree very well with those of Bary, although experimental data unfortunately are lacking in the latter case.

For the sake of completeness it should be added that the exact calculation of the viscosity, taking all correction factors into account, is not possible, because estimation of the Reynolds number for the Höppler viscometer, of the same Reynolds number for the particles, and the influence of the wall on the Höppler viscometer are not yet possible. Because irregular currents are in motion in the vicinity of the gap, it is quite conceivable that in the Höppler viscometer the various influences compensate one another in a favorable way, and for this reason the results agree with the simple viscosity formula of Guth.

It has already been pointed out that, in making viscosity measurements of diluted latex, it is unimportant whether water or dilute ammonia is added. It has been shown further that the viscosity of 60 per cent latex with about 1 per cent of ammonia, based on the aqueous phase, does not change in any significant way when the ammonia is driven off by means of a current of nitrogen to the point where only 0.1 per cent remains. The decrease in viscosity which should take place when

natural latex is treated with ammonia is therefore not reversible, and this leads to the conclusion that this decrease in viscosity is brought about by chemical changes, probably decomposition of albumin.

For a long time it has been the practice in the oil and artificial silk industries to

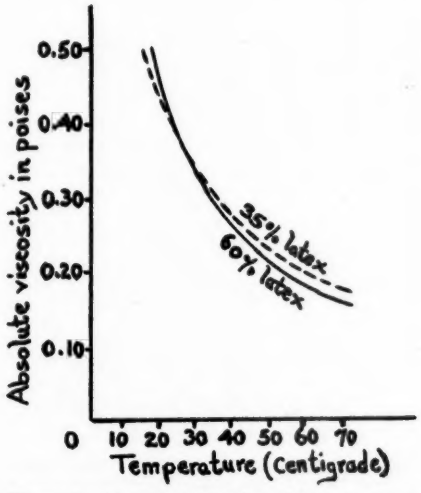

Figure 3—Absolute Viscosity of 35 and 60 Per Cent Latex at 15 to 70 °C.

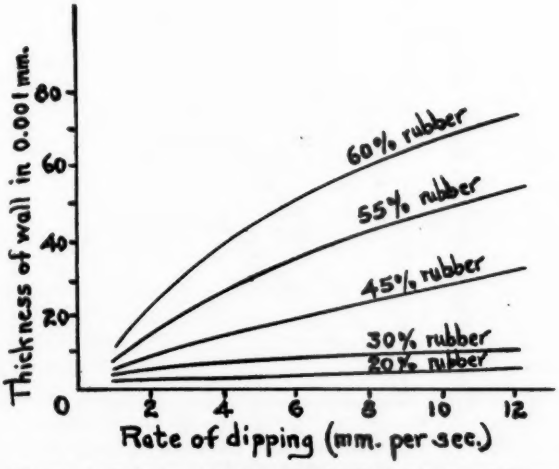

Figure 4—Relation between the Wall Thickness of Latex Films and the Concentration of Rubber and Rate of Dipping

use viscosity data for characterizing their products. It is therefore certainly not amiss, in marketing the raw material latex as well, to take into account the viscosity, not only because viscosity determination gives easier control of uniformity and variations in individual shipments, but also because the viscosity is of importance from the point of view of the future use of latex. In addition to measuring

the viscosity, it is advisable to determine the content of dry solids and of ammonia, and also to estimate the stability. Obviously there should be an examination of the

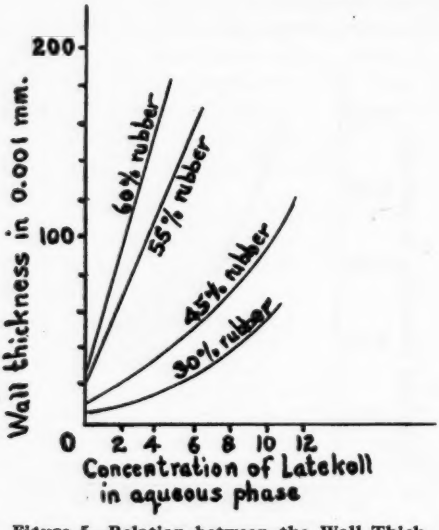

Figure 5—Relation between the Wall Thickness of Latex Films and the Concentration of Latekoll and of Rubber. (Rate of Dipping 3 mm. per Sec.)

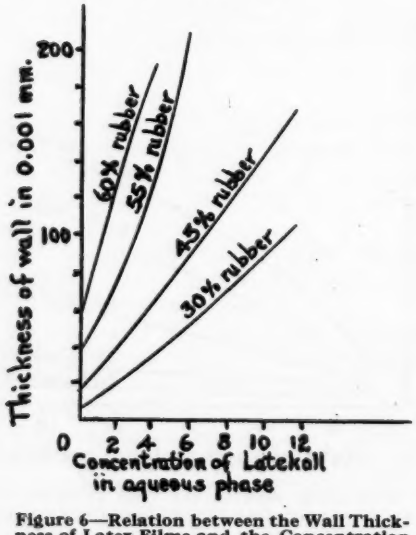

Figure 6—Relation between the Wall Thickness of Latex Films and the Concentration of Latekoll and of Rubber. (Rate of Dipping 6 mm. per Sec.)

general appearance and color. The viscosity method is also suitable for determining changes in latex during long periods of storage. Thus typical experiments have shown that, during storage for three months, the viscosity of a shipment of latex

diminished from 0.65 to 0.61. Probably during this time further transformation of the albumins took place.

For the standardization of dipping mixtures a knowledge of the viscosity of latex is of great importance. The thickness of the wall of the articles to be dipped depends on the following factors: (1) on the length of the form; (2) on the rate of immersion; (3) on the solid content of the mixture; (4) on the viscosity of the mixture.

The relation between the rate of dipping and the thickness of the wall of the dipped article is evident in Fig. 4. This diagram likewise shows the relation between solid content and thickness of wall. The relations between viscosity and wall thickness are shown in Figs. 5, 6, and 7. Here the abscissas do not represent the viscosities, but rather the proportions of the latex-thickening agent, Latekoll (based on the aqueous phase), which are proportional to the viscosity. The curves

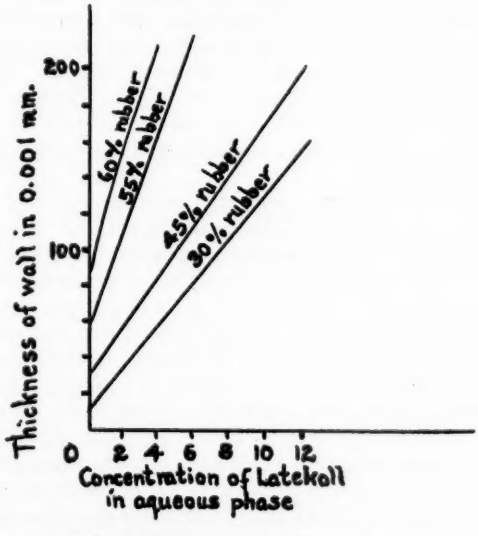

Figure 7—Relation between the Wall Thickness of Latex Films and the Concentration of Latekoll and of Rubber. (Rate of Dipping 12 mm. per Sec.)

were drawn from latex-Latekoll mixtures containing 30, 45, 55, and 60 per cent rubber at three different rates of dipping, *i. e.*, 3, 6, and 12 millimeters per second, as is customary in practice. The Latekoll content made practically no difference in the total content of solids, because Latekoll itself is an aqueous solution.

Viscosity data are purposely omitted, and the corresponding quantities of Latekoll are shown instead for the reason that difficulties are encountered in the precise measurement of the absolute viscosities of latex mixtures thickened to such extents. An examination of the experimental data from this point of view, with special attention to sources of errors, showed that when the viscosity was doubled in the range of 0.05–0.5, the wall thickness increased 50 to 100 per cent. These average increases in wall thickness were true for rates of dipping between 3 and 12 millimeters per second, and for latex concentrations between 30 and 60 per cent.

The experiments were carried out with pure latex-Latekoll mixtures, because it would have been difficult to choose, among many possible complete dipping mix-

tures, those of the most general interest. Maintenance of a uniform viscosity for latex mixtures to be used in spreading operations is just as important as it is for dipping operations. It might therefore be of value in the preparation of mixtures for spreading, as in the preparation of those for dipping, to carry out control tests by some reliable and simple means of measurement of the viscosity of the raw material and of the mixture ready for spreading.

This immediately raises the question as to how the viscosity desired in a latex mixture can be obtained. Assuming that a latex of a definite concentration is available, there are in principle two ways in which the desired viscosity may be obtained: (1) by increasing the content of dry solids, based on the water phase, and (2) by increasing the viscosity of the water phase. The viscosity can be kept under control fairly exactly by either of these methods, and the choice of method depends on the use to which the latex is to be put. If it is a question of thickening an uncompounded latex, only the second method is applicable, in which case a water-soluble high molecular compound such as pectin, gum tragacanth, or Latekoll, can be added. This method makes it possible to increase the viscosity of highly concentrated latices considerably by small additions of reagent. It should be noted in this connection that water-soluble substances of this character not only increase the viscosity of the water phase, but probably also increase the viscosity of the whole system by being in part adsorbed on the surface of the rubber particles, thus increasing the size of the latter.

Evidence in favor of this last assumption can be obtained in the following manner. It is known that water-soluble, colloidal substances bring about creaming. This creaming phenomenon cannot be explained theoretically by a change in viscosity, because the establishment of the so-called sedimentation equilibrium is independent of the viscosity. The sedimentation equilibrium is, on the contrary, a function of the third power of the radius of the particles, and since by addition of the agents mentioned the only influence tending to disturb the equilibrium is a change in the radius of the particles, creaming is probably attributable only to adsorption. As would be expected if adsorption takes place, the clear serum which separates as a result of creaming necessarily has a considerably lower viscosity than it would have if all of the creaming agent were dispersed uniformly in the serum. For example, 500 cc. of 35 per cent latex (from 292 cc. of 60 per cent latex and 208 cc. of water) and 27 cc. of water containing 3 grams of creaming agent A creamed in 3 days, and gave a serum having a viscosity η_r of 17.5; 117 cc. of 1 per cent NH_3 + 235 cc. of water + 3 g. of creaming agent A gave after 3 days' standing a serum having viscosity η_r of 39.7.

In loaded mixtures also the use of a thickening agent is quite practicable. However, in this case it is at times of advantage to reduce the cost of the mixture by further loading in addition to the thickening agent. This of course involves an impairment of quality. The choice of filler to bring about the desired thickening is of prime importance, as is evident from the different thickening effects obtained with various types of kaolin. Since it is always necessary to add some liquid along with the filler to the latex in order to prevent coagulation, the thickening effect obtainable is limited.

Aside from the two processes which have been described, it is possible to increase the viscosity of latex, though in a still uncontrollable way, by the addition of substances which bring about thixotropy. It is not possible to give any general recipe, because the appearance and the intensity of the thixotropic effect depends on the composition of the mixture. Latex stabilized by ammonia becomes thixotropic if it contains at the same time mercaptobenzothiazole and zinc oxide, or the antioxidant MB and zinc oxide. Bentonite also is known to bring about thixotropy.

It is difficult or almost impossible to add these substances in such proportions that a definite viscosity is obtained, and moreover the slightest mechanical action lowers the viscosity considerably, and therefore in the course of processing latex undergoes permanent changes in viscosity.

Finally, incipient vulcanization leads to an increase in the viscosity of latex, so that this phenomenon also can be utilized to regulate viscosity. However, it is impossible to stop the viscosity at the desired point, and then again the time element is not within control. Changes in viscosity by incipient vulcanization, which of course is not the only contributing cause of changes in the viscosity of latex, lead to another quite different and complicated problem of the greatest importance, *viz.*, to maintain the viscosity of a latex mixture at a constant value.

In addition to the effect of incipient vulcanization, the viscosity of a latex mixture is changed by various other influences, including evaporation of water and ammonia; heat; mechanical influences such as friction, agitation, and stirring; and the specific effects of active substances; precipitating ions, etc. All these causes, including incipient vulcanization, lead finally to coagulation of the latex mixture. The rate at which this final result is reached varies greatly, so that cases of spontaneous coagulation as well as thickening during a period of several weeks are to be found.

Latex can and must be protected from these various influences, and this may be accomplished by adequate protection of latex mixtures during storage, storage in a cool place, protection against mechanical influences by stabilizing agents such as alkalies, casein and Vultamol, and protection against active substances and precipitating ions by other special stabilizing agents.

That incipient vulcanization in latex mixtures should lead to increases in viscosity, as in solutions of rubber, is really surprising. In a rubber solution in which the individual solvated rubber molecules, which are separated from one another, are united by vulcanization with sulfur, there is quite naturally a decrease in the solubility, and therefore a tendency to gel. In latex the disperse phase, the rubber, is not in the form of individual molecules; rather, the dispersoid particles are compact aggregates of a large number of rubber molecules. On the assumption that rubber has a molecular weight of 50,000, it can be calculated that a latex particle consists of about 5,800,000 molecules of 1 μ diameter. In view of the considerable distance which separates the particles from one another, and the enveloping layer on the latex particles (according to Bary 0.07–0.09 μ), it is extremely improbable that the latex particles react with one another during vulcanization, and it must be assumed that the vulcanization reaction takes place only within the individual latex particles. There seems then to be no direct cause for a change in viscosity as a result of incipient vulcanization in a latex mixture. In view of this, the thickening of a complete latex mixture must be attributed to the independent effects of sulfur, zinc oxide, and accelerator on the colloidal system. At variance with this assumption, however, are two facts. First, as shown by the experiments in the present work, all vulcanizing agents must always be present together, and secondly, the rate of thickening, the strength or activity of the accelerator, and the rate at which incipient vulcanization appears, bear a close relationship to one another. A very active combination of accelerators, such as a mixture of piperidinium pentamethylenedithiocarbamate and hexahydroethylaniline hexylethyldithiocarbamate (Vulkacit P + Vulkacit 774), brings about incipient vulcanization, and at the same time rapid thickening, *i. e.*, within a few days. With weaker accelerators, such as zinc phenylethyldithiocarbamate (Vulkacit P extra N) or tetramethylthiuram disulfide (Vulkacit Thiuram), incipient vulcanization and, correspondingly, thickening take place more slowly. If physical effects, and not incipient vulcanization,

Table I

Influence of the Concentration of Ammonia on the Behavior of Latex Mixtures

The mixture contained: 60 per cent latex, 165; 85 per cent colloidal sulfur, 2.35; zinc phenylethyldithiocarbamate, 0.8; 10 per cent Vultamol, 5; Latekoll, 0.50; active zinc oxide, 0.65 and 2 (as shown below). Each horizontal group of three values gives the tensile strength (in kg. per sq. cm.), the percentage elongation at break, and the stress (in kg. per sq. cm.) at 700% elongation.

		NH_3 0.94 Per Cent						NH_3 2 Per Cent						NH_3 3 Per Cent					
		ZnO 0.65			ZnO 2			ZnO 0.65			ZnO 2			ZnO 0.65			ZnO 2		
Hot air at 100° C.	30 min.	227	1042	42	296	1050	56	250	1042	57	242	983	61	232	1033	53	211	900	78
	55 min.	200	1017	..	250	1008	58	211	983	61	225	942	74	250	1025	55	211	900	78
Vulcanization of Test Rings A at room temperature. Rings prepared from mixture one day old	After 2 days	116	1050	33	94	958	35	135	1058	44	125	942	49	87	917	37	112	925	50
	4 days	110	1042	35	128	1017	39	206	1067	49	181	983	56	182	1058	44	177	1017	57
	8 days	183	1117	39	210	1133	47	230	1025	57	240	1067	56	230	1025	57	209	975	72
	16 days	252	1133	42	250	1150	44	221	950	66	250	967	73	211	933	57	232	917	76
	24 days	223	1117	36	261	1117	43	225	1000	54	225	1000	58	210	967	53	194	917	73
Vulcanization at room temperature. Test Rings B prepared after the number of days specified. Tested after 24 hours	After 2 days	116	1050	33	94	958	35	135	1058	44	125	942	49	87	917	37	112	925	50
	4 days	146	1033	48	136	967	50	114	950	46	138	992	52	107	917	44	110	933	44
	8 days	163	925	62	149	892	67	133	958	47	127	967	49	126	1017	41	148	983	54
	16 days	164	867	77	172	925	64	89	875	42	110	958	46	114	1050	34	122	992	45
	24 days	144	900	71	131	817	82	116	1033	37	98	917	45	110	1033	33	103	1033	39
Viscosity, determined by the falling bulb viscometer, in seconds	After 1 day	0.2			0.2			0.2			0.2			0.2			0.2		
	8 days	0.4			0.2			0.2			0.2			0.2			0.2		
	21 days	0.5			0.2			0.2			0.2			0.2			0.2		
	42 days	1.1			0.2			0.2			0.2			0.2			0.2		
	70 days	7.5			0.3			0.3			0.3			0.3			0.3		
Percentage change in length after swelling 24 hours in benzine	After	A		B	A		B	A		B	A		B	A		B	A		B
	2 days	140		140	140		140	140		140	140		140	140		140	140		140
	4 days	140		140	140		140	140		140	140		140	140		140	140		140
	8 days	100		100	100		100	60		140	60		140	60		140	60		140
	16 days	80		80	80		80	80		140	60		140	60		140	60		140
	24 days	80		80	80		80	60		100	60		100	60		100	60		100

Table II

Influence of the Concentration of Ammonia on the Behavior of Latex Mixtures

The mixture contained: 60 per cent latex, 165; 85 per cent colloidal sulfur, 2.35; zinc diethyldithiocarbamate, 0.8; 10 per cent Vultamol, 5; Latekoll, 0.33; special zinc oxide, 0.65 and 2 (as shown below). Each horizontal group of three values gives the tensile strength (in kg. per sq. cm.), the percentage elongation at break, and the stress (in kg. per sq. cm.) at 700% elongation

		NH_3 0.94 Per Cent						NH_3 2 Per Cent						NH_3 3 Per Cent					
		ZnO 0.65			ZnO 2			ZnO 0.65			ZnO 2			ZnO 0.65			ZnO 2		
Hot air at 100° C.	45 min.	250	1033	61	210	925	73	211	958	71	213	900	81	219	987	77	218	867	100
	60 min.	220	967	63	230	942	83	203	850	77	232	917	97	227	908	95	206	833	114
Vulcanization of Test Rings A at room temperature. Rings prepared from mixture one day old	After 2 days	90	883	38	103	933	35	89	858	46	114	900	56	79	833	46	93	867	57
	6 days	70	850	40	93	950	38	81	883	45	101	950	42	110	900	48	67	758	54
	13 days	186	1125	39	168	1042	42	160	1067	43	155	1025	46	142	917	53	152	933	72
	24 days	222	1042	62	237	1000	74	214	992	77	225	1000	85	207	967	82	207	925	98
Vulcanization at room temperature. Test Rings B prepared after the number of days specified. Tested after 24 hours	After 2 days	90	883	38	103	933	35	89	858	46	114	900	56	79	833	46	93	867	57
	6 days	80	833	54	101	833	64	84	867	45	81	825	57	60	742	49	71	708	60
	13 days	170	883	94	201	892	113	123	900	45	114	850	63	133	958	59	114	833	72
	24 days	166	892	74	148	808	111	145	867	71	120	875	67	108	867	55	99	825	60
Viscosity, determined by the falling bulb viscometer, in seconds	After 2 days	0.2			0.2			0.2			0.2			0.2			0.2		
	6 days	0.2			0.2			0.2			0.2			0.2			0.2		
	13 days	1.0			0.4			0.2			0.2			0.2			0.2		
	24 days	7.0			0.8			0.4			0.4			0.2			0.2		
	42 days	50.0			3.0			0.4			0.4			0.2			0.2		
Percentage change in length after swelling 24 hours in benzine	After	A		B	A		B	A		B	A		B	A		B	A		B
	2 days	140		140	140		140	140		140	140		140	140		140	140		140
	6 days	140		100	140		100	140		140	140		140	140		140	140		140
	13 days	140		100	140		100	140		140	140		140	140		140	140		140
	24 days	60		60	60		60	60		80	60		80	60		120	60		100

were alone responsible for the gradual thickening, then a relation of this kind between the activity of an accelerator and the rate of thickening would not be expected. In such case it would probably be reasonable to assume that if thickening were the result only of the effect of the individual ingredients which had been added, one would necessarily expect that, with increase in the concentration of zinc oxide, thickening would be hastened, for zinc oxide is known to exert a sensitizing action on latex. However, as is evident from earlier published work,[7] latex mixtures with a zinc oxide content of 0.6–0.8 thicken in the shortest time. This latter fact may be considered as evidence that thickening is not a result of the independent effects of the various ingredients, but rather the combined action of these ingredients, as is vulcanization. A satisfactory explanation of the relationship between incipient vulcanization and thickening can of course not yet be offered, but investigations of this problem are now in progress.

The dependence of the rate of thickening on the zinc oxide content, just mentioned, shows at once the possibility of preparing more stable latex mixtures by adjusting the zinc oxide content to the most favorable concentration. Then again by the addition of suitable stabilizing agents, thickening can be retarded for any given conditions of incipient vulcanization.

A further possibility of maintaining the viscosity of a latex mixture at a constant value is that of retarding incipient vulcanization itself. As the result of a study of incipient vulcanization in latex mixtures, it was found that in general it occurred more rapidly in a latex mixture than it did in the same mixture previously dried at room temperature directly after preparation. Water-soluble accelerators had an unfavorable, *i. e.*, an accelerating effect on the rapidity with which incipient vulcanization occurred. In general, accelerators insoluble in water gave more favorable results; the best results were found with zinc salts of dithiocarbamic acids, such as zinc phenylethyldithiocarbamate (Vulkacit P extra N) and zinc diethyldithiocarbamate.

With these last two accelerators, incipient vulcanization could be greatly retarded, without vulcanization of the dried mixture being influenced to any noteworthy extent, either at room temperature or at elevated temperatures, by increasing the ammonia content of the latex mixture. The ammonia content, based on the water phase, is ordinarily about 1 per cent, but by increasing this to 2–3 per cent, incipient vulcanization in latex mixtures containing these accelerators can be retarded three- or four-fold, and a corresponding increase in the stability and thus a more nearly constant viscosity can be attained. Furthermore ammonia itself has a direct stabilizing effect. Tables I and II summarize the results of experiments on incipient vulcanization with zinc phenylethyldithiocarbamate and zinc diethyldithiocarbamate, and with various proportions of ammonia. Incipient vulcanization was estimated by swelling experiments, and also by measuring the mechanical properties. In these latter tests, account had to be taken of the fact that latex, even when unvulcanized, has considerable tensile strength and elastic modulus compared to masticated rubber.

An examination of the tabulated data makes it evident that with increase in the ammonia content (1) incipient vulcanization in a latex mixture is retarded and the mixture is rendered more stable, and (2) the behavior on vulcanization of a latex, especially vulcanization in hot air, is not affected to any considerable extent by the ammonia content. Only a slight stiffening effect is noticeable.

In experiments with other accelerators, such as a mixture of piperidinium pentamethylenedithiocarbamate and hexahydroaniline cyclohexylethyldithiocarbamate (Vulkacit P + Vulkacit 774) or methyl pentamethylenedithiocarbamate, as well as

in experiments with other bases in place of ammonia, such as methylamine and sodium hydroxide, no such pronounced effect was found.

If then it is possible to prepare latex mixtures containing ultra-accelerators with but a slight tendency to incipient vulcanization only with zinc salts of dithiocarbamic acids, it is still of advantage in many cases to be able to modify and control incipient vulcanization in latex mixtures. The effect of ammonia is probably attributable to the fact that with the accelerator it forms complexes which are difficultly soluble in rubber, and which diffuse into the rubber particles in quantities sufficient to bring about vulcanization only after their decomposition by drying.

By using weaker accelerators, stable latex mixtures which require higher temperatures and longer times to vulcanize are readily obtained. Among these relatively mild accelerators which give stable mixtures in which incipient vulcanization appears very slowly, are tetramethylthiuram disulfide (Vulkacit Thiuram), which occupies an intermediate position, Vulkacit TR, a mixture of mercaptobenzothiazole (Vulkacit Mercapto) and Vulkacit TR, and finally Vulkacit AZ. Obviously mercaptobenzothiazole also belongs to this group, but it should be mentioned that under some conditions this accelerator in the presence of zinc oxide causes thixotropy, so that a constant viscosity is not obtained.

Within the bounds of this work on the viscosity characteristics of latex and of latex mixtures, it has been possible to deal in many cases only with experimental results, and not with the details of experimental conditions or with the task of showing the various ways in which this particular property of latex, its viscosity, can and must be taken into account.

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The Preservation of Latex by Acids

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Introduction

This note describes the results of some purely empirical attempts to preserve field latex by the simple addition of acid. Common knowledge of the process of coagulation and published researches thereon do not encourage the view that acids might be used to maintain field latex in a fluid condition over long periods. Fullerton (*Quart. J. Rubber Res. Inst. Malaya*, **2**, 156 (1930–31)), in coagulation experiments, found that when latex containing 20 per cent by weight of rubber is treated with progressively increasing amounts of acid, the second liquid zone—which, with latex containing 4 per cent of dry rubber, occurs between the p_H values 3.52 and 1.00—is barely if at all apparent. With undiluted field latex containing 35 per cent dry rubber, this second liquid zone is entirely absent; between the p_H values 4.49 and 0.83, which represent amounts of added acid corresponding to 2 cc. and 30 cc. of NHCl per 100 cc. latex, coagulation is either complete or almost complete, and no zone of complete dispersion is found. From these experiments it would appear very unlikely that by the addition of any acid to field latex, fluidity could be maintained. The results obtained in some such experiments with large amounts of acid are described below.

Experimental

Trials with Acetic Acid.—Experiments were first made with latex diluted to a dry-rubber content of 15 per cent. In Fullerton's experiments (*loc. cit.*) with such latex, the greatest amount of acetic acid applied was 8 cc. of the 2.5 per cent acid or roughly 0.2 cc. of the pure substance per 100 cc. of latex. With amounts of acid of this order, complete coagulation resulted. In the present experiments it was found that if the amount was increased to between 10 cc. and 20 cc. of pure acid per 100 cc. latex, no coagulation occurred, and fluidity was maintained during an observation period of over three weeks.

When similar experiments were made with latices containing over 30 per cent dry rubber, however, coagulation or clotting resulted over a wide range of acid concentrations. Nowhere in the range which extended to 25 cc. of pure acid per 100 cc. of field latex was a zone of satisfactory fluidity observed.

Trials with Formic Acid.—With this acid, fluidity zones were found both for diluted and undiluted field latex.

It was found that with latex diluted to a dry-rubber content of 15 per cent, a fluid condition was maintained for over six weeks by the addition of amounts of 90 per cent formic acid lying in the zone 5–25 cc. per 100 cc. of latex.

With undiluted field latex, fluidity was maintained for the same period on treatment with between 7 and 25 cc. of 90 per cent acid per 100 cc. latex. The fluidity zone appeared, however, to be narrower with some latex samples than with others. In certain cases the upper limit beyond which coagulation occurred, either immediately or in less than three days, was found to be 15 cc. of acid per 100 cc. of latex. The amount giving the best general results was the equivalent of 10 cc. of 90 per cent acid per 100 cc. latex. Samples of field latex preserved with this amount of

acid were found after six weeks, storage to have no putrefactive odor; the latex also passed through a sieve having 100 meshes per inch without leaving measurable clots. There was, however, a noticeable lack of stability; when heavy frothing was induced by vigorous agitation the froth coagulated. Similarly, rapid stirring quickly induced coagulation in the body of the latex. After approximately eight weeks' storage in glass a clear yellow serum began to appear in the lower layers of latex; shaking restored homogeneity but partial separation occurred again in approximately one week's time. This indicated almost beyond doubt that the acid-preserved latex was in a micro-flocculated condition, which would account in great measure for its comparative instability. It was found that the stability of the latex could be improved slightly by the addition of 1 per cent of saponin, calculated on the rubber phase of the latex. Curiously enough casein had little if any stabilizing effect. The saponin-"stabilized" latex, although less sensitive to added compounding solids such as sulfur and zinc oxide than the parent unstabilized acid latex, was nevertheless decidedly unstable.

Trial shipments to England of the simple and saponin-"stabilized," formic acid-preserved field latex in four-gallon lots were received and reported on by the technical officers of the London Advisory Committee for Rubber Research. It was found by these officers that with the simple formic acid latex an appreciable amount of clotting took place on the walls of the containers during transit, and that in the case of the saponin-"stabilized" latex the amount of clotting was almost negligible. Further confirmation of the Malayan observations on stability was forthcoming in the fact that the acid latices proved much too unstable for normal compounding in England.

Trials with Hydrochloric, Nitric, and Tri-chloracetic Acids.—Preliminary trials with abnormally large amounts of these acids on undiluted field latex have so far not resulted in the finding of zones of permanent fluidity for latices treated with them.

Discussion and Summary

It is shown that by the application to field latex of amounts of formic acid of the order of 9 per cent by weight of the latex or 10 per cent by volume of the 90 per cent commercial acid, a product results which will retain its fluidity for long periods. It is, however, apparently micro-flocculated, and unstable. Because of their instability, it seems unlikely that acid latices of this kind will find technical applications. The findings are in no way contradictory to those of Fullerton, whose experiments on coagulation did not include trials with such large amounts of acid.

It is regretted that fuller experimental data cannot be given because most of the relevant records were destroyed recently by fire at the Institute. It is probable that a further study will be made, from which additional experimental data together with a possible explanation of the empirical observations given here may emerge.

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The Viscosity of Raw Rubber

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Introduction

Eyring[1] has recently published a theory of the viscosity of both simple and non-Newtonian liquids. This work is based on recent developments in the theory of homogeneous reaction velocities.[2] The latter theory was initiated by the well-known Arrhenius equation for the velocity constant of a reaction:

$$k = Ae^{-B/RT}$$

Here A and B are constants characteristic of the reaction, R the gas constant, and T the absolute temperature. The constant A depends on the spatial requirements which must be fulfilled by the reacting molecules. B equals the average energy of the reacting molecules minus the average energy of all the molecules, and is spoken of as the "activation energy" of the reaction. The newer theoretical work has enabled the calculation of both the factor A and the activation energy, using the straightforward methods of statistical mechanics. In the applications of the theory to condensed systems, the molecular force fields are not, in general, sufficiently well known to permit quantitative predictions of reaction velocity. In principle, however, the calculations may be carried through. Since it is not possible to make a detailed application of the theory of reaction rates to problems of viscosity, further outline of this theory will be omitted.

The contribution which Eyring has made to the theory of viscosity lies in his recognition of the fact that in many cases flow takes place by means of activated, that is to say, energy-rich molecules. The phenomenon may therefore be treated by the same methods which have been shown to be successful in describing velocities of chemical processes. Although the foregoing has been recognized with varying degrees of clarity by a number of earlier investigators,[3] Eyring has expressed the relationships in a more concrete form and, in addition, has shown how the viscosity depends on shearing stress in certain cases of non-Newtonian fluids.

The discussion proceeds as follows. The average molecule in a liquid is confined by van der Waals forces to a region of low potential energy. When, in the course of statistical fluctuations about this average state, the molecule acquires thermal energy in excess of the average, it may escape from the potential "hole" to an adjacent potential minimum. It should be noted that this picture of the liquid state bears a closer analogy to the situation existing in solids than to that which obtains in the gaseous state. This point of view is well established through a variety of theoretical work. In the case of a liquid which experiences no external unbalanced forces, the jumping of the molecules from one potential minimum to another takes place uniformly in all directions, so that there is no net flow. If, however, a shearing stress is applied to the fluid, it has the effect of lowering the activation energy in one direction and increasing it in the reverse direction. In other words, the applied stress pulls the molecules out of the potential holes in one direction, and makes it more difficult for them to jump in the reverse direction. There is, therefore, a net flow of the fluid.

We may calculate the viscosity of the system in the following manner. Consider

a fluid confined between two planes, $z = 0$ and $z = Z$. The upper plane moves with uniform velocity in the direction of increasing x. We assume that a laminar flow is set up in the fluid. By definition:

$$\eta = f/(dV/dz) \tag{1}$$

where η is the viscosity of the fluid, f the shearing stress, and V the velocity of the layer, parallel to the x, y plane, and at a height z. dV/dz may be expressed for our purposes as $\Delta V/\lambda_1$, where λ_1 is the distance between two adjacent layers, and ΔV is the difference in velocity between these two layers. The rate of flow in the forward direction will then equal the fraction of molecules which are activated times the frequency with which they jump, times the distance they go in each jump. This is expressed by the following equation:

$$\text{Velocity of forward flow} = k_0 \exp\left\{-\frac{E_0 - {}^1/_2 f\lambda_2\lambda_3\lambda}{kT}\right\} \cdot \frac{kT}{h} \cdot \lambda \tag{2}$$

Here k_0 is the equilibrium constant expressing the number of activated molecules in proportion to the total number of molecules, but neglecting the activation energy. The exponential term takes account of this latter factor. Here E_0 is the depth of the potential hole (the activation energy in the absence of shearing stress) and the quantity ${}^1/_2 f\lambda_2\lambda_3\lambda$ is the work done by the applied force in assisting the molecule out of the potential hole. λ_2 and λ_3 are the dimensions of the molecule along the X and Y directions, respectively. Their product, therefore, gives the cross section on which the applied force acts. k is the Boltzmann constant (gas constant per molecule) and T is the absolute temperature. The fraction kT/h, where h is Planck's constant, expresses the frequency with which the activated molecules jump. λ is the distance each molecule jumps.

Similarly, the rate of flow in the reverse direction may be written:

$$\text{Velocity of backward flow} = k_0 \exp\left\{-\frac{E_0 + {}^1/_2 f\lambda_2\lambda_3\lambda}{kT}\right\} \cdot \frac{kT}{h} \cdot \lambda \tag{2'}$$

Subtracting these, we obtain for the net velocity of the layer under consideration with respect to a layer λ_1 centimeters away:

$$\Delta V = k_0\lambda \frac{kT}{h}\, e^{-E_0/kT} \cdot 2\sinh\frac{f\lambda_2\lambda_3\lambda}{2kT} \tag{3}$$

By substitution we obtain the following expression for η:

$$\eta = {}^1/_2 f \frac{\lambda_1}{\lambda}\frac{1}{k_0}\frac{h}{kT}\, e^{E_0/kT}/\sinh\frac{f\lambda_2\lambda_3\lambda}{2kT} \tag{4}$$

Eyring has given a brief discussion of the application of this equation to Newtonian liquids. In this case ${}^1/_2 f\lambda_2\lambda_3\lambda \ll kT$. Expanding the sinh, and neglecting all terms of higher power than the first, Eyring finds:

$$\eta = \frac{\lambda_1 h}{k_0} \cdot \frac{1}{\lambda_2\lambda_3\lambda^2}\, e^{E_0/kT} \tag{4a}$$

He then shows that this expression gives results equivalent to those obtained from the empirical equations of Andrade and of Batschinski when applied to non-associated liquids. It should be noted that, as must be the case, f does not appear in Equation 4a. In words the viscosity of a Newtonian liquid is independent of the shearing stress.

The application of Equation 4 to non-Newtonian liquids is of importance in the present discussion. Let us consider the case when $^1/_2 f\lambda_2\lambda_3\lambda \gg kT$. Then:

$$\sinh \frac{f\lambda_2\lambda_3\lambda}{2kT} \approx \exp \frac{f\lambda_2\lambda_3\lambda}{2kT}$$

In practice the above approximation is valid if $f\lambda_2\lambda_3\lambda/2kT \geq$ about 1.5. Equation 4 then becomes:

$$\eta = f \frac{\lambda_1}{\lambda} \frac{1}{k_0} \frac{h}{kT} \exp \left\{ \frac{E_0 - {}^1/_2 f\lambda_2\lambda_3\lambda}{kT} \right\} \tag{4b}$$

which may be rewritten in the form:

$$\eta = Afe^{(a-bf)/T} \tag{5}$$

Here, of course, f does appear in the equation.

There are very few data in the literature of sufficient scope to enable a test of this equation, with the exception of some recently published figures obtained by Mooney.[4] These data were obtained by means of the rheometer. They describe the viscosity of a sample of pale crepe (after milling for 5 minutes) as a function of temperature and shearing stress. The present paper contains a check of Eyring's theory by means of Mooney's data, and an interpretation of the data in terms of the theory.

Procedure

The constants in Equation 5 necessary to give the best fit with the experimental data were obtained as follows. First the equation was rearranged to the form:

$$\log_{10} \eta/f = \log A + (a - bf)/2.3T \tag{6}$$

A preliminary plot of $\log \eta/f$ *vs.* $1/T$ was made, and the slope of each line adjusted so as to give an approximately linear relation of slope with shearing stress. The values of the slopes were then plotted against the shearing stress and extrapolated to zero stress. This curve gave the values for a and b. The constant A was obtained from the individual curves of the preliminary plot, neglecting the points corresponding to the lowest and highest values of shearing stress, since it was obvious that the former did not fit the equation, and since the latter were too scattered to be taken into account for the present purpose. It should be mentioned that it is not possible to fit the lowest shearing-stress curve and also those of intermediate stresses by manipulation of the three constants of Equation 5. The values of these constants for this particular sample are:

$$A = 1.65 \times 10^{-4}$$
$$a = 5.10 \times 10^{3}$$
$$b = 1.28 \times 10^{-5}$$

The extent of the agreement is shown in Fig. 1, in which $\log \eta/f$ is plotted against $1/T$. The points are Mooney's experimental data and the lines are given by Equation 5 using the above values for A, a, and b.

Discussion

The discrepancies between calculated and observed values are no greater than the possible experimental error (neglecting the curve of lowest shearing stress), with the possible exception of the data for the highest shearing stress. These latter may represent either a permanent change in the rubber, or the limit of the applicability of Equation 5. Further experimental work will be necessary to settle

this point. Discussion of the curve for lowest shearing stress will be postponed for the moment.

Constant b.—From Equation 4a it is seen that b equals $\lambda_2\lambda_3\lambda/2k$. If we assume that the distance jumped by the molecule is equal to the length of the molecule, $\lambda_2\lambda_3\lambda$ may be expressed as a volume per molecule or mole. This volume is equal to 3.52×10^{-19} cc. per "molecule," or 2.13×10^5 cc. per "mole." This assumption is surely not valid in the case of a rubber molecule. It seems much more probable that the distance jumped is of the order of magnitude of a small multiple of the length between two double bonds. If this is the case, the cross section of the moving particle is much greater than that of a rubber molecule. It may therefore be concluded that the moving particle in slightly masticated rubber consists of a cluster of hydrocarbon chains rather than an individual molecule.

Constant a.—Since a has been found to be equal to 5100, E_0 is readily calculated to be 10.2 kcal. per "mole." This seems a rather large activation energy to be caused by van der Waals attractions, judging from the temperature coefficient of the viscosity of low molecular liquids. In the present case E_0 is large because of the large size of the moving particle.

Constant A.—According to the theory of reaction rates this constant is given by the expression:

$$A = H(\lambda_1/\lambda)(F_n/F_a^*)(h/kT) \qquad (7)$$

Here H is a "transmission coefficient" expressing the probability that the molecules, being in a state satisfying both energy and spatial requirements, will react, that is to say in the present case, jump from the potential minimum. For our purposes, this constant may be assumed with considerable certainty to equal unity. λ_1 and λ have been previously defined. F_n and F_a^* represent, respectively, the partition functions of the normal and of the activated molecules. These quantities have been defined and discussed by Fowler.[5] In the Darwin-Fowler statistical theory they play the same role as does the "volume of the phase space" in Gibbs' theory. Substituting the value for the known constants in the expression for A we find that:

$$H(\lambda_1/\lambda)(F_n/F_a^*) = 1.31 \times 10^9.$$

This is an extremely large number compared to the corresponding quantities for simple liquids, for which values ≈ 1 are found. It seems most probable that this behavior is due to rather stringent spatial requirements on the moving particle. These requirements mean that the probability of the activated state is much less (apart from energy considerations) than the probability of the normal state. In other words, the moving particle must be favorably oriented. It is also possible that the distance jumped by the moving particle is considerably less than the distance between the moving layers. This would mean that the particle goes a distance much less than its average diameter in the course of a single jump. Probably both these factors are of importance in determining the order of magnitude of the factor A.

The foregoing discussion has neglected entirely the nonhomogeneity of crude rubber. It has been shown by Grenquist, Hauser and Hünemorder, and others[6] that some of the latex particles of raw rubber persist throughout 60 to 90 minutes of mastication. The present sample had much less breakdown. It seems unlikely that the moving particle can be identified with the latex particle, since we would then expect still larger values for the constant b and smaller values for the constant A. This conclusion is not, however, of great certainty; it would take much more experimental data of the type here discussed in order to settle the question. In

particular, it would be desirable to follow the change in the constants of Equation 5 with mastication of the rubber, and also to determine them for purified rubber.

That these calculations definitely indicate a moving particle larger than the rubber molecule might be cited as evidence for the existence of the much discussed rubber micelle. Such a citation seems unjustified if we adopt a more reasonable definition of the term "micelle" than is generally used. This is of course an arbitrary matter, since there is no well-defined usage for this term. In its broadest sense, a micelle is defined as a clump of molecules held together by van der Waals forces. If we use this definition, it is necessary to regard water as a micellar liquid, and therefore as a colloidal system. This seems a thoroughly unjustifiable extension of the domain of colloidal chemistry, not because of any desire to limit the boundaries of this field of knowledge, but because of the fact that "colloidal" methods of experimentation and discussion have not yielded results of benefit in the investigation of associated liquids. It seems preferable to delimit the colloidal field, and the term micelle, to systems which are definitely of a two-phase nature, and to employ those statistical methods which have been fruitful in other fields in an attack upon associated one-phase systems, whether they be composed of one or many components.

Under the present interpretation, rubber hydrocarbon is an associated organic liquid. The association is, however, not caused by intense van der Waals forces, as is the case with water and other simple fluids, but is due to the mechanical interlocking of long hydrocarbon chains. Association in high polymeric hydrocarbons is therefore a secondary effect of the primary valence forces, and does not depend primarily on van der Waals forces. Regarding the plastic phenomena of rubber from the point of view of the molecular constitution of this substance, it seems most natural that the molecules of raw rubber should be so much entangled that they move as groups or clusters.

The fact that the data obtained by Mooney for the lowest shearing stress do not agree with the theory is probably to be ascribed to changes in the rubber produced by the shearing stress. It is to be noted that the activation energy under these conditions is correctly given by Equation 5, since the calculated line is closely parallel to the observed points. The factor A is too small to give agreement with experiment, however, by a factor of about two. This may be due to a partial orientation by the shearing stress of the rubber as a whole. In order for this explanation to hold, it is necessary for the partial orientation to be more complete at the higher shearing stresses than at the lowest. Such a behavior would not be particularly surprising. An alternative explanation may be that the moving particles are partly broken up at the higher shearing stresses, so that the quantity λ_1 of Equation 7 is decreased.

Another way of accounting for the increase of A found experimentally at the lowest shearing stress, would be to assume that the distance jumped increases with increasing stress. If this behavior becomes pronounced, the particle can no longer settle down into the next energy minimum; one or more minima must be passed over. When this is the case, the present theory is inadequate to account for the behavior of the system, since under these circumstances viscous resistance by momentum transfer becomes important. This process is familiar from the customary analysis of the viscosity of gases. With a slight revision of the mental picture (free path $<$ molecular diameter) it may be applied to liquids. This has been done by Jaeger, and more recently by Andrade.[7] Between the limiting cases of very high and very low stresses there will be of course a transition region. From the data now under discussion, it is not possible to specify just where this transition

from viscous loss by activation to loss by momentum transfer takes place for rubber. It is quite probable, however, that it occurs within the higher stresses used in the experiments. To settle questions of this type will require a theory taking account of both activation and momentum transfer. The omission of the latter phenomenon in the present theory accounts for the prediction of Equation 5 that the viscosity becomes zero at very high stress. This can hardly be expected to be the case.

Throughout these calculations the jumping of molecules in the direction opposite to that of the applied stress has been neglected. This seems hardly justifiable at the lowest temperature and stresses, since here $(bf)/T$ is only about 1.3. Sub-

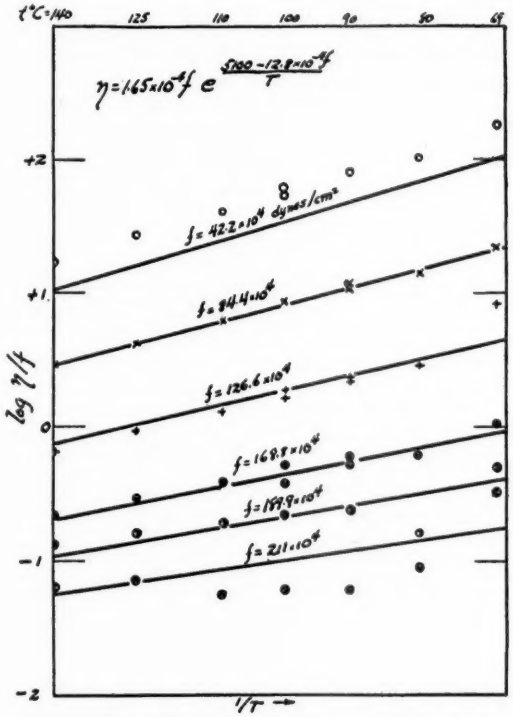

Figure 1—Plot of Log n/f *vs.* $1/T$ for a Sample of Pale Crepe after Milling for 5 Minutes

stitution of the hyperbolic sine for the exponential term (use of Equation 4 instead of Equation 5) brings the topmost curve of Fig. 1 slightly closer to the experimental points, but does not remove the discrepancy. It is interesting, however, that these measurements extend nearly to the range in which it is necessary to consider the reverse flow as well as the forward flow.

A further point to be noticed is that the present treatment assumes that the number of activated particles is not so large that their motion disturbs the thermal equilibrium of the system. There is no *a priori* way of calculating the range of validity of this assumption. From chemical reaction velocities, it seems fairly safe in the present application, but if it were not, the system would be in the transition region discussed above and Equation 5 would not apply.

In conclusion, we may say that Eyring's equation is a satisfactory first step in giving a kinetic description of the viscosities of non-Newtonian systems such as rubber. It is to be hoped that an extension of the theory will be possible.

I wish to express my thanks to M. Mooney and R. H. Gerke for a number of discussions concerning this work, and to W. A. Gibbons, Director of these laboratories, for permission to publish this paper.

Summary

1. Eyring's equation for the viscosity of a non-Newtonian fluid describes Mooney's data satisfactorily for all except the lowest shearing stress.

2. From the standpoint of the present theory, the behavior at low shearing stresses may most readily be explained by any of the following assumptions: (1) the moving particle is larger at low than at high shearing stresses; (2) the rubber as a whole is less oriented by the lower shearing stress; (3) the distance "jumped" at the low shearing stress may be less than that at high stresses.

3. According to the present interpretation, the moving particle (corresponding to the molecule of a simple liquid) is larger than the rubber molecule. It does not seem profitable to interpret this finding as evidence for the existence of a rubber micelle.

4. Both the activation energy of viscous flow for this particular sample of rubber, and the factor determined by the spatial requirements which must be fulfilled by the moving particle, are much larger than the analogous quantities for low molecular hydrocarbons.

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The Effects of Elastic Stretch on the Infrared Spectrum of Rubber

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Previous studies of the infrared absorption of rubber have been made by Stair and Coblentz[1] and by Williams.[2] Stair and Coblentz observed a small band at 6μ and an intense band near 12μ, in addition to the usual hydrocarbon bands at 3.4μ, 7.0μ, and 7.3μ. An interesting study of the effects of aging (oxidation) was carried out by these authors, and it was found that marked increases in absorption occurred at 2.8μ, at 6.0μ, and in the region between 7μ and 12μ. Williams obtained transmission data for several types of latex rubber and compared the spectra of these materials with those of related hydrocarbons, such as isoprene and styrene. It was found that the small absorption band observed at 6μ by Stair and Coblentz was actually a complex band having several maxima. The results obtained were in fair agreement with the Raman data obtained by Gehman and Osterhof[3] in their studies of solutions of rubber compounds, although the Raman studies revealed the presence of a number of minor frequencies which did not appear in the infrared work.

It has been suggested by a number of writers that the mechanism of elastic stretch is intimately connected with the structure of the rubber molecule, and a theory has been developed by Mack[4] which accounts for stretch and retraction in terms of a rotation about single bonds in the isoprene polymer. That profound changes take place in the structure of rubber when stretched has been revealed by x-ray studies,[5] which show that the diffraction patterns of unstretched rubber consist of the diffuse bands characteristic of liquids, while the patterns of stretched rubber are well defined as in the case of crystalline substances. Other evidences of radical changes in structure accompanying stretch are the variations in optical properties which occur.[6] It was suggested that further infrared studies might be of value in obtaining additional information concerning the mechanism of stretch. Hence it was decided to obtain transmission curves for rubber under different conditions of stretch in an effort to detect any changes that might occur.

The spectrometer used in the present work, a prism instrument of the minimum deviation type, was designed by the authors and constructed in the local Drake laboratory shop. The mirrors, of focal length 230 mm., are 40 mm. in diameter. The rocksalt prism, obtained from Kipp and Zonen, has a refractive angle of 60° and refracting faces 40 mm. by 72 mm. In order to protect the prism from moisture, all but the refracting faces were covered with a thick layer of a water-proof cement, while these were lacquered with an extremely thin layer of pyroxylin in amyl acetate. A Kipp and Zonen compensated thermopile of 18 junctions, used as a radiation receiver, was connected to a Leeds and Northrup galvanometer of sensitivity 0.01μ V per mm. for the scale distances used. The extreme steadiness of the zero point made it possible to use small deflections, since the shift of zero reading was seldom greater than one or two millimeters per hour. The air deflections varied from 12.0 cm. near 3μ to 2.8 cm. in the water vapor band at 6μ. The actual slit widths used were: 0.005 cm. between 2μ and 4.5μ, 0.010 cm. between 4.5μ and 6.5μ, and 0.015 cm. between 6.5μ and 8.0μ. In the earlier part of

the work an optical relay system using a photronic cell was employed, but mechanical vibrations in the building made it necessary to discard the amplifier. In taking the transmission data, about 16 readings per μ were taken in the 3μ region and 24 per μ at 7μ. After the spectrum had been mapped carefully, fewer readings were taken, but these were concentrated in regions of particular interest. In making the wave-length calibration curve, Paschen's values[7] for the indices of refraction were used, the theoretical curve being checked experimentally by means of the sodium *D* lines, the water vapor bands, the carbon dioxide bands, and the bands of liquid water, alcohol, and benzene. There are but slight discrepancies between band positions determined in this manner and those obtained in previous work[2] by means of the Hilger calibrated drum. There is close agreement between the present results and those obtained by Stair and Coblentz.[1]

A wide range of materials was studied in the present investigation, and the writers are especially grateful to S. D. Gehman, R. H. Gerke, and Lewis Larrick for their kind coöperation in furnishing samples. The materials, which had of necessity to be reasonably clear and free from surface irregularities, ranged from uncured latex rubber to vulcanized rubber with sulfur content as high as 10 parts of sulfur to 100 parts of rubber hydrocarbon. As far as the method of cure is concerned, it was found that the effects about to be described are to a large extent independent of the cure except that the compounds containing high sulfur concentrations are unable to withstand sufficient stretching to make the results significant. The material found best suited for use in this study was a type of sheet-latex rubber containing about one per cent of zinc oxide and stearic acid. In all, the complete spectra from 2μ to 8μ were obtained for some fifty-five samples of rubber under different conditions of stretch, while transmission data in regions of special interest were obtained in about thirty other cases. To provide unilateral stretch, flat brass plates 10 cm. apart were fastened to an ordinary absorption cell holder, and clamped the rubber firmly after the desired elongation had been obtained. Layers of felt between the clamps and rubber provided better contact and prevented slipping while the observations were being made. The effects of local strains due to the clamps were minimized by allowing the radiation to pass through the middle of the sample. The measurements of the lengths were made with an ordinary centimeter scale; the large sizes of the samples used made such a method of measurement sufficiently accurate.

Several mechanical devices for producing radial stretch were designed and tested. However, it was found that the most satisfactory results were obtained by stretching the sheet rubber over a wide metal ring of large diameter and holding it in place by means of a strong rubber band. A small circle was printed on the unstretched rubber, and the sheet was stretched until this circle mapped into a larger concentric circle of the desired size. In cases where extremely large increases in area were desired, it was found necessary to use several successive reference circles, since the width of the lines defining the original circle became too wide to permit accurate measurements. In all cases care was taken to prevent the appearance of regions of local strain in the samples. Measurements of thickness were made with a micrometer gage, and readings were taken when the pressure on the sample had reached a definite value, determined by the ratchet. Repeated tests on the sample taken on different days indicate that the readings taken in this manner could be repeated satisfactorily. On any one sample a number of determinations of thickness were made and the average used.

In Fig. 1 are indicated the results obtained for unilateral stretch. The curves in Fig. 1 (*a*) represent the transmission of a single layer under different tensions. Curve *A* shows the transmission of an unstretched layer 0.045 mm. in thickness.

It will be noted that in this curve there are regions of strong absorption with maxima at 3.26μ, 7.10μ, and 7.35μ, while weaker bands appear in the 6μ region. It has been found that in different samples of unstretched rubber the exact positions

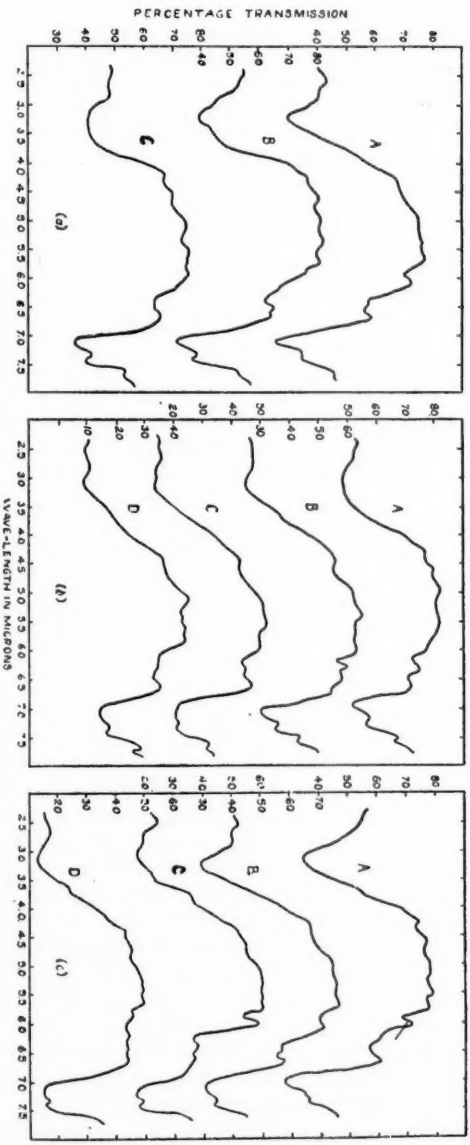

Figure 1—The Transmission of Rubber under Various Conditions of Unilateral Stretch

of the maxima vary slightly, the exact position depending in part on the thickness and in part on the condition of the surfaces. In unstretched materials the positions of the apparent maxima vary from 3.2μ to 3.4μ, 6.9μ to 7.1μ, and 7.3μ to 7.4μ

respectively. It will be noted that two less intense absorption maxima appear at 5.9μ and at 6.5μ. These less intense bands appear in the regions where one would expect the fundamental linear vibrations of C=C and the first harmonics of C—C to produce absorption. The complex absorption in this region is radically affected by stretching. However, owing to the relatively low resolution and the small galvanometer deflections obtainable in this region, little definite information could be gained on this subject. It may be well to point out at this point that there are a large number of minor absorption bands in the rubber spectrum between 4μ and 6μ. These bands, which appear as small depressions of five or six per cent in the transmission curve, were thought at first to arise from interference effects such as those described by Ellis in his studies of Cellophane.[8] However, since the positions of these minor bands remain approximately the same when different thicknesses are studied, the writers are inclined to believe that they are true absorption bands and are possibly harmonics of bands appearing at longer wave-lengths. Evidences for absorption of this type were also found in previous studies.[2]

Curves *B* and *C* of Fig. 1 (*a*) represent the transmission of the same sample after it had been stretched unilaterally until the thicknesses of the absorbing layers were 0.030 mm. and 0.023 mm., respectively. Several marked changes are apparent. The 3.25μ band becomes broader, and its center of absorption is shifted to longer wave-lengths with increasing stretch. The 7μ absorption bands also become broader, while the 7.35μ band becomes more intense compared with the 7.1μ band. However, the most interesting point observed is that the general absorption is appreciably greater in the case of the stretched samples. Thus, we find the transmission at 3.25μ and at 7μ in curve *C* only 10 per cent higher than in curve *A*, while the general absorption at 5μ is actually greater for curve *C*. The fact that the thickness of the sample whose transmission is indicated in curve *C* is actually only half that of the sample used for curve *A* would lead one to expect changes greater than those observed. It is evident that the absorbing properties of rubber become greater when the material is under tension. In the 6μ region the intensity diminishes appreciably with increasing stretch.

The possibility that the observed effects might be only apparent, arising from variations in thickness alone, led to the study of a number of different thicknesses of sheet rubber experiencing the same percentage elongation. Some of the results are indicated in Fig. 1 (*b*), where the curves *A*, *B*, *C*, and *D* represent transmission data for thicknesses of 0.014 mm., 0.030 mm., 0.045 mm. and 0.063 mm., respectively. All the samples used in obtaining the curves shown in this part of the figure were experiencing an elongation of approximately 300 per cent. It will be noted that the bands at 3μ and 7μ become broader with increasing thickness, as one would expect. The observed increase in the intensities of the bands and of the general absorption is to be expected. When these curves are compared with the transmissions of the same thicknesses of unstretched rubber, it is found that the absorption is greater in the case of the stretched samples.

Comparisons of the transmission of layers of equal thickness (0.045 mm.) under different conditions of stretch are given in Fig. 1 (*c*). In the curves *A* and *B* are shown the spectra of samples under zero tension before and after stretching, a few minor variations appearing at 3.2μ and near 6μ. Curves *C* and *D* represent the transmission of samples having the same thickness when experiencing 100 and 300 per cent elongations, respectively. These curves make even more pronounced the general effects noted in connection with the curves of Fig. 1 (*a*).

The transmission spectra of rubber experiencing radial stretch are shown in Fig. 2 (*a*). Curve *A* represents the transmission of the unstretched layer 0.045 mm. in thickness. Curves *B*, *C*, and *D* represent the spectra of the same sample after the

area had been increased 100, 200, and 300 per cent, respectively, by radial stretching. As in the case of unilateral stretch, the general absorption becomes greater and the major bands become broader with increasing stretch. One point of special note is the manner in which the 3.2μ region of absorption becomes broader as elongation increases. A second maximum appears near 3.5μ, and becomes more pronounced as stretching continues, while the maximum originally present at 3.2μ is apparently shifted to slightly shorter wave-lengths. If stretching is continued until the sample is 7 or 8 times the original area, the 3.5μ depression often becomes even more pronounced than the one at 3.2μ. In the case of radial stretch, the small bands appearing in the 6μ region become less intense than those in the spectra of unstretched and unilaterally stretched rubber, and are completely absent in some samples. There are small shifts in position of the maxima in the 7μ region, but these slight shifts can scarcely be considered of great significance, since there is considerable overlapping of the principal bands in this region.

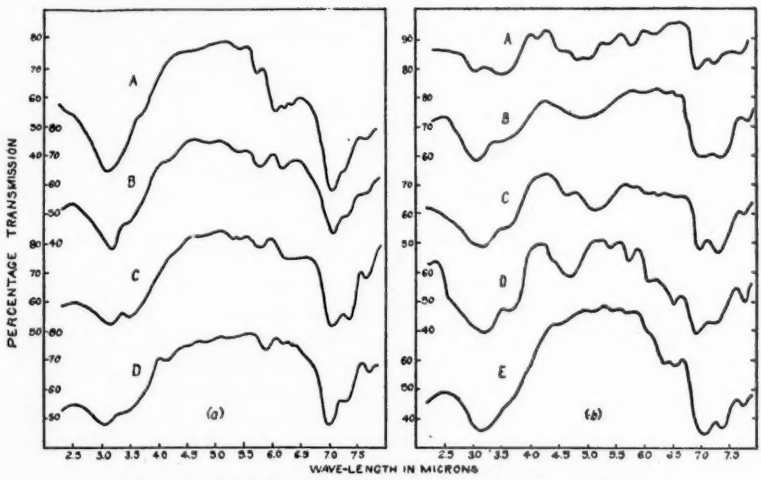

Figure 2—The Transmission of Radially Stretched Rubber

It was observed that when samples of rubber were stretched radially to the limit—11 to 13 times the original area in most cases studied—an intense absorption band appeared near 4.8μ, a spectral region in which there is no strong absorption in unstretched rubber. Spectra of stretched specimens showing this band are given in Fig. 2 (*b*). In curve *A* this band appears at 4.7μ and is nearly as intense as the bands in the 3μ and 7μ regions. In curve *A* the 3.5μ absorption is more intense than the band appearing at 3.15μ. In curves *B* and *C* the additional band appears near 4.8μ. The center of the band appearing in curve *B* lies at 4.85μ, while in curve *C* the band appears as a double band with one maximum at 4.65μ and the second at 5.10μ. The rubber used in obtaining these transmission curves was a cured type containing about one per cent of zinc oxide and stearic acid and one per cent of sulfur. It was suggested that the band appearing near 4.8μ might arise from a sulfur-carbon vibration, since a band appears at this position in the spectrum of carbon disulfide.[9] In order to test this point, sheets of uncured latex rubber were stretched radially to the limit—about 7 or 8 times the original area—and their transmissions measured. Stretching uncured rubber radially to this

degree without tearing was rather difficult. Data had to be taken immediately after the specimen was prepared, since flow was quite rapid in most cases. The results obtained with one sample are shown in curve D, in which an intense absorption band appears at 4.7μ. The band was obtained for several uncured samples, but that shown in curve C is more intense than in most of the others. It was found that, after samples had been stretched for several hours, the natural flow was sufficient to relieve the tension, and the effects of stretch disappeared from the spectrum. The final curve in the figure, curve E, is the transmission curve of an unstretched layer of rubber 0.045 mm. in thickness and is included for purposes of comparison.

In determining the transmission of a substance like rubber a number of effects are involved. As in the case of any transmission spectrum, the selective reflection and the selective absorption are the predominant phenomena concerned. However, one must consider other effects such as diffuse reflection, scattering by surface irregularities, and also scattering and reflection by particles within the body of the material being studied. In order to determine the causes of the changes in the rubber spectrum which accompany stretch, it is necessary to gain an idea of the relative variations in these effects. The surface phenomena, including general, diffuse, and selective reflection will enter into the transmission equation in the form of a coefficient, since their magnitudes in no way depend upon the thickness of the sample under consideration. The true absorption and the body scattering, however, depend on the thickness of the sample, and hence appear in the exponential factor of the transmission relation. Thus, we may write the ordinary equation in the form:

$$I = (1 - \rho)I_0 e^{-\alpha t}$$

where I represents the measured intensity of the transmitted radiation, I_0 the intensity of the incident radiation, and t the thickness of the absorbing layer. The coefficient ρ is the term arising from the surface effects and the term α in the exponent is a measure of the true absorption plus body scattering.

By measuring the thicknesses t_1 and t_2 and the intensities I_1 and I_2 of the radiation transmitted by two different specimens under similar conditions, it is possible to gain an idea of the relative contributions of the surface and body phenomena by solving Equations 1 and 2 for ρ and α.

$$I_1 = (1 - \rho)I_0 e^{-\alpha t_1} \quad (1)$$

$$I_2 = (1 - \rho)I_0 e^{-\alpha t_2} \quad (2)$$

Involved in this procedure are difficulties which are immediately apparent. One of these lies in the inaccuracies involved in determining the thickness of a substance having properties like those of rubber; the methods described above and employed in the present study are open to criticism. A more serious difficulty arises from the questionable assumption that the term ρ, which involves surface irregularities, is the same even for samples taken from the same sheet, since there is no method of estimating the variations introduced in the interdependent terms ρ and α.

Measurements were made on a number of samples which enabled α and ρ to be determined as a function of percentage stretch. In Table I are given the values of these constants obtained in the representative spectral regions: 3.35μ, 5.5μ, 7.1μ, and 7.35μ. It will be noted that in every spectral region considered, the body coefficient α increases with increasing stretch, while the surface factor ρ decreases with stretch. These changes are similar for radial and unilateral stretch. Owing to the variations introduced by differences in the surface conditions of any one

pair of samples, the exact values of ρ and α vary within certain limits, even for samples taken from the same sheet of rubber, but the changes with stretch are in the same direction for all specimens considered, and are indicative of a definite trend which shows the body coefficient for 600 per cent stretch to be roughly three times as great as that for unstretched rubber. The observed changes in the

TABLE I*

A. UNILATERAL STRETCH

Per Cent Stretch	3.3μ		5.5μ	
	α	ρ	α	ρ
000	10.3	0.22	0.5	0.21
100	17.7	0.29	2.0	0.18
200	20.8	0.27	6.0	0.09
300	36.2	0.11	11.5	0.05
400	34.0	0.14	12.2	0.03
500	27.0	0.11	10.0	0.02
600	26.0	0.13	10.0	0.03
	7.7μ		7.1μ	
	α	ρ	α	ρ
000	10.0	0.51	7.4	0.66
100	23.1	0.29	28.2	0.31
200	27.5	0.25	25.1	0.20
300	36.3	0.17	25.0	0.19
400	40.0	0.20	34.0	0.15
500	24.0	0.24	20.0	0.26
600	32.0	0.16	30.2	0.18

B. RADIAL STRETCH

Per Cent Stretch	3.25μ		5.5μ	
	α	ρ	α	ρ
000	10.3	0.54	4.5	0.10
100	12.3	0.48	5.8	0.12
200	18.0	0.40	9.0	0.08
300	13.7	0.35	14.5	0.07
400	23.3	0.26	11.0	0.07
500	42.2	0.14	13.5	0.05
600	30.0	0.23	10.0	0.07
	7.1μ		7.3μ	
	α	ρ	α	ρ
000	7.9	0.59	6.0	0.64
100	8.2	0.58	23.2	0.36
200	18.0	0.40	37.2	0.19
300	23.7	0.29	35.0	0.20
400	30.0	0.23	30.0	0.22
500	36.0	0.23	29.9	0.25
600	30.0	0.30	33.3	0.21

* The values given in the table are accurate to approximately 10 per cent.

body coefficient with stretch are much greater than those predicted on the basis of the known variations of density.[10] The accuracies of α and ρ given in Table I are based on the errors involved in the determinations of transmission and thickness and should not be taken to indicate the probable error, obtained from a large number of observations. The data shown are the values as obtained from two representative samples under various tensions.

In view of the observed doubly refracting properties of stretched rubber,[6] it was suggested that these properties might in some way account for the observed changes in the body coefficient. Although the incident light experiences only one reflection before reaching the absorption cell position, the radiation undergoes five

reflections in passing through the spectrometer, and hence is slightly polarized by the time it reaches the thermopile. In obtaining the data for the unilaterally stretched rubber, every sample was placed in the light beam with the direction of stretch the same. However, tests showed no appreciable change in transmission when the direction of stretch was varied. Therefore it is doubtful that the observed changes in body coefficient can be attributed directly to double refraction.

Although a purely theoretical interpretation of the vibration spectrum of a highly polymerized material like rubber is impossible, it may nevertheless be possible to draw some inferences on the basis of the empirical relationships developed by a number of investigators.[11] Thus, since bands have been found in the same positions in the spectra of large numbers of organic compounds, it has been possible to attribute the 3.35μ bands to a linear vibration of CH bonds and the 7μ bands to deformation frequencies of CH_2 and CH_3 groups. Of course, all the bands arise from normal vibrations of whole molecules, but their frequencies are largely determined by the natural vibrations of certain groups and it has become customary to speak of the frequencies involved as though they actually arose from particular groups. Thus, one may consider the broadening of the 3μ band with increasing unilateral stretch as being the result of new constraints placed directly on the CH bonds, or as being the effect of other radical changes in the rubber structure which cause variations in the normal frequencies of the molecules. Since the shift of the band position is towards longer wave-lengths, it is apparent that the stresses are such as to cause lower vibrational frequencies to be assumed by a large number of the absorption units present. The broadening of the 7μ region of absorption and the relative increase in the intensity of the 7.3μ component in unilaterally stretched samples are further evidence of lower frequencies in the case of stretched rubber. The x-ray work of Hauser and Mark[5] shows that unilaterally stretched rubber gives rise to a spot diffraction pattern superimposed on the amorphous ring characteristic of unstretched rubber. Since the positions of the spots remain unchanged with increasing stretch, it is concluded that they arise from a definite space lattice. The intensity of the spots increases with the tension, while the intensity of the amorphous ring decreases. The conclusion drawn from these x-ray observations is that in the process of stretching there is a gradual transition from a liquid (amorphous) phase to a crystalline phase. From the diffraction patterns Hauser and Mark find evidence of a typical fiber structure. It is probable that the units possessing the lower frequencies observed in the present work are those in the crystalline lattice, since these units are influenced to a greater extent by their immediate neighbors.

In the radial stretch data the variations in the 3.3μ and 7μ bands are similar to the changes accompanying unilateral stretch in that broadening takes place and that the intensity of the bands is greater. However, there is no pronounced shift towards longer wave-lengths in either band. The 3.3μ band, which is double when the material is stretched radially, is different in shape from the band observed in unilaterally stretched rubber. The center of the region of absorption near 7μ remains practically unchanged in position, since the higher frequency component shifts to shorter wave-lengths and the 7.3μ band increases in intensity. As mentioned above, little significance can be attached to the shifts of the maxima of the individual components in this region, since overlapping occurs, and the shape of the measured transmission curve is hence dependent on thickness. There is, however, ample evidence of changes in the rubber structure which are different from those observed in the case of unilateral stretch. The intensity of the complex absorption near 6μ was noticeably diminished by radial stretch; further study of this region under high dispersion might prove valuable. The appearance of the

broad bands near 4.8μ in the spectra of radially stretched samples gives additional evidence of structural change. From the results obtained in the present study, it is impossible to ascribe this absorption at 4.8μ in the spectra of radially stretched samples to any definite group. The band was observed in the spectra of a number of specimens of different thicknesses, and its intensity is so great that it is doubtful that it can be attributed to interference effects. Since the x-ray results indicate the existence of a ring structure[5] in radially stretched rubber, it is possible that the 4.8μ band arises from one of the units in this type of lattice. The lattice in radially stretched rubber is markedly different from the fiber structure caused by unilateral stretch.

In ordinary rubber there are two types of hydrocarbons present: the sol or alpha-rubber and the gel or beta-rubber. These hydrocarbons are distinguished by their different solubilities in ether, and are thought by most writers to represent different degrees of polymerization of the isoprene units. In the interpretation of the early x-ray results it was suggested that the characteristic crystalline diffraction patterns were caused by the beta component, the relative amount and regularity of arrangement of which was supposed to be increased by stretching. However, when it was discovered later that crystalline patterns could be obtained by stretching pure alpha-rubber, some doubt was cast upon the earlier interpretation. Stair and Coblentz found the spectra of alpha- and beta-rubber identical up to 9μ. Thus, the changes in the rubber spectrum observed in the present investigation offer further evidence that the crystalline component of stretched rubber cannot be identified with beta-rubber.

TABLE II

Compound	State	$\alpha_{CH} \times 10^{21}$	Note
C_2H_2	Gas	1.5	Triple Bond
C_2H_4	Gas	1.6	One Double Bond
$(CH_3)_2O$	Gas	1.9	Methyl Ether
$(C_2H_5)_2O$	Gas	1.7	Ethyl Ether
$C_{10}H_{20}$	Liquid	2.0	One Double Bond
$C_{12}H_{24}$	Liquid	2.3	One Double Bond
$C_{15}H_{30}$	Liquid	1.9	One Double Bond
$C_{16}H_{32}$	Liquid	1.9	One Double Bond
$C_{18}H_{38}$	Liquid	2.1	One Double Bond
$C_{24}H_{48}$	Liquid	2.1	One Double Bond
$C_{19}H_{36}$	Liquid	2.0	One Double Bond
$C_{22}H_{24}$	Liquid	2.0	One Double Bond

	Per Cent Stretch	Unilateral $\alpha_{CH} \times 10^{21}$	Radial $\alpha_{CH} \times 10^{21}$
Rubber	000	0.9 to 1.8	0.9 to 1.8
	100	2.1 to 2.6	1.5 to 2.1
	200	2.2 to 3.3	1.8 to 2.6
	300	4.1 to 5.2	1.9 to 3.0
	400	4.4 to 5.3	3.0 to 4.0
	500	4.0 to 5.2	4.4 to 5.0
	600	3.9 to 5.2	4.4 to 5.2

It was noted above in the discussion of absorption and reflection effects that the coefficient α, which included the true absorption and body scattering, became larger with increasing stretch, and for a stretch of 600 per cent was approximately three times as great as for zero stretch. To have a check on the values obtained, it was decided to compare the values of the coefficients with the absorption coefficients of other organic compounds. Since the band near 3.3μ is simpler in structure than any of the other characteristic bands observed, it was chosen for comparison with the corresponding bands in the spectra of other unsaturated

hydrocarbons. The data of Coblentz[12] were chosen for use in making the comparison, since large numbers of compounds were studied under the same conditions and with the same methods. To have a common basis for comparison, it was necessary to compute the effective absorption coefficients per CH bond in the

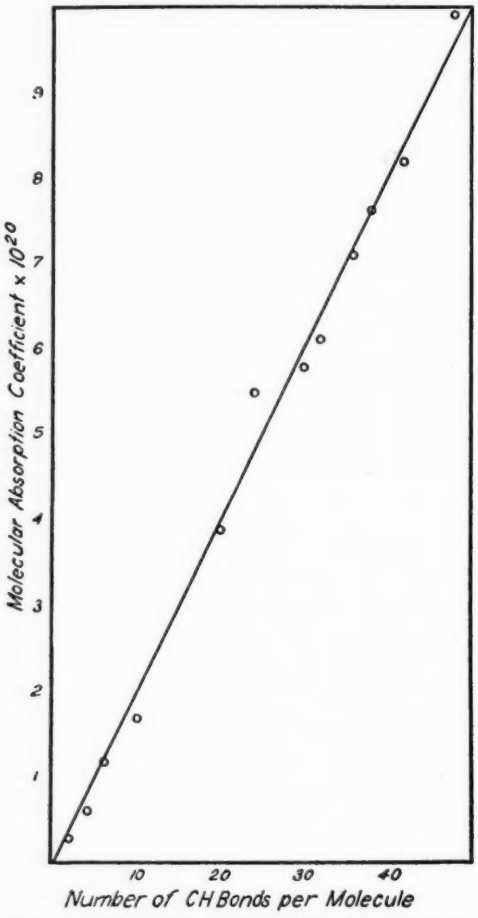

Figure 3—The Absorption Coefficient per Molecule of Various Unsaturated Hydrocarbons in the Region of 3.3μ as a Function of the Number of CH Groups per Molecule

following manner. If α is the absorption coefficient per centimeter of thickness, we may obtain the absorption per molecule α_M by the relation:

$$\alpha_M = \alpha M/\rho N$$

where M is the molecular weight, ρ the density, and N Avogadro's number. Then, on dividing α_M by the number of CH bonds per molecule, one may obtain the coefficient per CH bond, which we will denote by α_{CH}. In Fig. 3 are shown the results obtained from Coblentz' work on unsaturated hydrocarbons; α_M is plotted

as a function of the number of CH bonds per molecule. It will be noted that the points approximate a straight line, the slope of which gives the average value of α_{CH} for the unsaturated hydrocarbons. In Table II are given the values of α_{CH} obtained for the individual compounds, and also the values of the body coefficient per CH bond obtained in the present study of rubber. The fact that the value of the body coefficient for unstretched rubber is in reasonable agreement with the values obtained for other hydrocarbons is an additional check on the accuracy of determinations of thickness made in the present work.[13] The values of α_{CH} for rubber experiencing a 600 per cent stretch are approximately three times as great as the values for unstretched rubber. There are two possible explanations tenable; the absorption per molecule may actually increase as a result of the stresses applied to the bonds themselves on stretching, or the apparent increase may arise from greater internal scattering caused by the creation of the crystal lattice in the body of the originally amorphous phase. From the results obtained thus far, it is impossible to determine which of these effects plays the more important role in producing the observed effects.

The writers wish to express their appreciation to F. H. Hayes and H. B. Messec for their aid in the construction of certain parts of the apparatus, and to the members of the physics staff for their interest in the work.

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The Oil Resistance of Rubber

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V. THE THERMAL EFFECT OF VAPORS ON RUBBER

This paper relates to the heat liberated by rubber when it is suddenly immersed in the vapors of various organic solvents. The quantity of liberated heat is affected by the polarity of the solvent. The measurement of this quantity should therefore offer a means of determining the polar properties of various rubber films, and thus of their oil resistance, as described in previous papers (*J. Soc. Chem. Ind., Japan*, **38,** 506B (1935); **39,** 138B, 319B(1936)). The usual solution method to determine molecular polarization cannot be applied to such materials as vulcanized, oil-resisting and synthetic rubbers which are not dissolved by non-polar solvents. The purpose of the present experiments is to ascertain the adaptability of the new method and its availability for the determination of the polar property of such materials.

Experimental

The thermal effect of vapors on rubber was first reported by Houghton (*Proc. Phys. Soc., London*, **35,** 39 (1922)). His paper, however, is rather brief, and lacks detailed descriptions of the experiments, the character of the rubber, and a discussion of the results. Since these experiments, no one has carried on a similar study. This paper is the first detailed one relating to the problem.

The apparatus consisted of three parts: A, B, and C, as shown in Fig. 1. All parts are connected by glass ground joints having mercury seals. A is a mercury manometer to measure the pressure in the system, B is a chamber which holds two test tubes D_1 and D_2, C is a container for the test liquid. The test tube D_1 is covered with a thin film of rubber by drying a rubber solution on the tube, while D_2 is left bare. A copper-constantan quadruple thermojunction is placed in the tubes to indicate the temperature difference between the two. The junction is connected to a sensitive mirror galvanometer through an external critical damping resistance. The apparatus is immersed in a water thermostat of $25 \pm 0.1°$ C. to water level W, to prevent condensation of vapor of the liquid in the apparatus. This is a very important precaution to obtain accurate and reproducible results.

Experiments were carried out in the following manner: Cocks C_1 and C_3 are shut, C_2 is opened, and all the system is evacuated by a mercury diffusion pump connected to P. Air below C_1 is evacuated to 0.001 mm. previously, so that the pressure in the chamber B may be determined by a manometer, A. Then cock C_2 is shut and C_3 opened. The vapor of liquid in C diffuses to B and touches the rubber film on D_1 and the glass surface of D_2. The rubber is suddenly heated, while the glass surface indicates no change. This temperature difference is observed by the movement of the beam of light from the mirror galvanometer. The time is measured with a stop watch until the beam returns to zero. Then C_2 and C_3 are shut, the vacuum pump is operated, and C_2 is opened slowly. As the solvent

vapor in chamber B is being pumped out, the desorption of solvent from the rubber film results in sudden cooling of D_1. In repeating the absorption and desorption, the maximum heat liberation occurred in the third or fourth absorption, as shown in Fig. 2. To convert the deflection of light beam to heat, the following calibra-

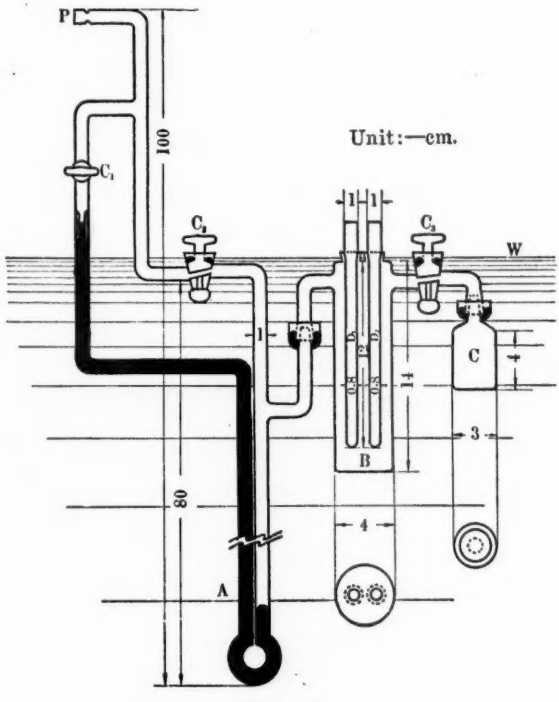

Figure 1

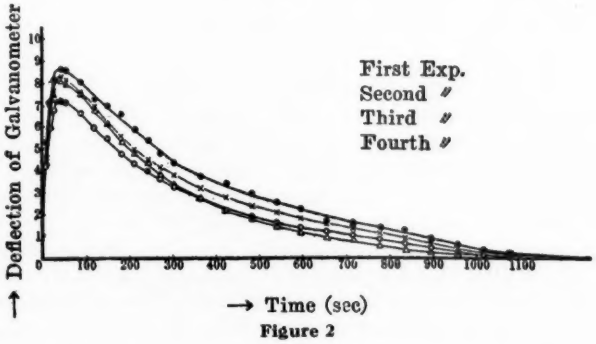

Figure 2

tion is carried out. A fine manganin wire (B. S. No. 38) is wrapped on the test tube D_1, and an electric current is supplied from a storage battery. This electric heating shows a deflection-time relation curve similar to that obtained in the heating resulting from the vapor absorption of the rubber film. The electric energy con-

sumed can be integrated easily. From the measurement of the area of the deflection-time curve obtained by the electrical heating, a factor to convert the deflection of the light beam of the galvanometer to heat quantity can be obtained by a planimeter. By this means, the heat liberated by one gram of rubber was measured for various solvents.

The rubber films were prepared by dipping the tube D_1 in a rubber solution and drying it in a vacuum desiccator. The rubber solution was a benzene extract of unpurified rubber which was obtained by coagulation of latex by acetone. This solution gives very satisfactory results for the physico-chemical study of crude rubber, as shown in the previous paper (*J. Soc. Chem. Ind., Japan*, **39**, 138B (1936)). The weight of the film was about 2 mg.; its thickness may be below 0.1 mm.

The heat liberated from rubber films in various liquids is shown in the following table.

TABLE I

Liquid	Grade of Liquid	Heat Liberated θ Cal./g. (Rubber)
Nitrobenzene	Kahlbaum. Ex. P. from crystal benzene	3.8
Acetone	Konishi. Ex. P.	54.7
Ethyl mercaptan	Katoh. Standard guaranteed	102.6
Ethyl acetate	Takeda. Ex. P. redistillation	94.4
1,4-Dioxan	Takeda. Ex. P. Sodium dist. 3 times	116.4
Cyclohexane	Theodor Schuchardt. P.	246.1
Ether	Kojima. Ex. P. Sodium dist. 2 times	303.8
n-Heptane	U. S. A. Fuel Committee	330.2
Benzene	Kahlbaum. zur Analyse. Sodium dist. 2 times, recrystallization. P_2O_5 drying	592.5
Carbon disulfide	Kahlbaum. P. zur Analyse	582.0
m-Chloroaniline	Dr. Frönkel. P.	27.0
Benzyl chloride	Kahlbaum. Ex. P.	20.8
Monochlorobenzene	Kahlbaum. P.	232.1
Ethylene dibromide	Takeda. P.	173.6
Ethylene dichloride	Kahlbaum. P.	1066.2
Chloroform	Kahlbaum. Ex. P. zür Analyse	703.9
Carbon tetrachloride	Kojima. Ex. P.	745.4
Methyl alcohol	I. G. P. Dist. 3 times	26.4
Ethyl alcohol	Takeda. Ex. P. for analysis	17.0
n-Propyl alcohol	Katoh. Ex. P.	12.7
n-Butyl alcohol	Takeda. Ex. P. Chemical	7.8

Theoretical Considerations

All vapors caused the liberation of heat as shown in the table above. When a rubber film is immersed in a vapor, several thermal phenomena may be detected, *e. g.*, heat of wetting, swelling, solvation, adsorption, and capillary condensation. Heat absorption occurs on immersion of rubber in benzene or toluene, as reported by several authors (Bostroem, *Kolloidchem. Beih.*, **26**, 439 (1928); Van Rossem, *Kautschuk*, **5**, 2 (1929); Sachse, *Gummi-Ztg.*, **43**, 2216 (1929); Hartner, *Kolloidchem. Beih.*, **30**, 83 (1929)). The amount of heat absorbed is several calories per gram of rubber. Hock reported that when rubber was immersed in benzene, toluene, and ethylene dichloride, the heat absorptions were 1.4, 0.4, and 0.5 calorie per gram, respectively, while chloroform and carbon tetrachloride showed heat liberation of 3.0 and 2.3 calories per gram. In any case, these examples show far smaller thermal effects than in the present experiments. The thermal effect in the present paper is assumed to be the sum of the heats of adsorption, capillary condensation, etc., in which the heat of capillary condensation is the predominant effect.

The heat of condensation ΔH can be expressed by the following equation:

$$\Delta H = RT^2 \frac{d \log P}{dT} \tag{1}$$

The heat of capillary condensation $\Delta H'$ is:

$$\Delta H' = RT^2 \frac{d \log P'}{dT} \tag{2}$$

where P is the vapor pressure of liquid over a plane surface and P' is that in a capillary. This vapor pressure can be derived by Kelvin's law, namely, $\log P'/P = 2\sigma M/RT\rho r$ (3), where σ is the surface tension of the liquid at $T°$ K., M is the molecular weight, ρ is the density of the liquid, and R is the gas constant. r is the radius of liquid drop or capillary. By expanding:

$$\log P'/P = \log[1 - (P - P')/P] = (P' - P)/P = P'/P - 1 \tag{3}$$

Hence

$$P' = P\left(1 - \frac{2\sigma M}{RT\rho r}\right) \tag{4}$$

Thus, P' in Equation 2 can be substituted by Equation 4, and the heat liberated by 1 mol. of liquid which condenses in a capillary having radius of r can be calculated. All values in this equation are obtained from Landolt-Börnstein Tabellen, the International Critical Tables and our observed data. However, the radius of the capillary is assumed to be 10 A. U. which is based on the dimension of the space between micelles of rubber.

Table II shows the observed amount of heat liberated per 1 gram of rubber

TABLE II

No. of Point in Fig. 3.	Liquid	θ Cal. per g. (Rubber)	$\Delta H'$ Cal.	θ/H' Mol.	Molecular Polarization of Liquid
Ordinary Compounds					
1	Nitrobenzene	3.8	49.8	0.06	353.8
2	Acetone	54.7	150.5	0.38	170.0
3	Ethyl mercaptan	102.6	125.3	0.82	147.
4	Ethyl acetate	94.4	97.6	0.97	92.0
5	1,4-Dioxan	116.4	78.2	1.49	26.0
6	Cyclohexane	246.1	104.8	2.35	28.
7	Ether	303.8	125.5	2.41	54.5
8	*n*-Heptane	330.2	81.4	4.06	34.55
9	Benzene	592.5	110.5	5.35	28.8
10	Carbon disulfide	582.0	122.4	4.76	22.2
Halogen Compounds					
11	*m*-Chloroaniline	27.0	55.9	0.48	213
12	Benzyl chloride	20.8	56.4	0.37	110
13	Monochlorobenzene	232.1	70.5	3.29	82
14	Ethylene dibromide	173.6	43.8	3.96	68
15	Ethylene dichloride	1066.2	87.6	12.17	57
16	Chloroform	703.9	76.5	9.21	49.8
17	Carbon tetrachloride	745.4	59.0	12.72	28.3
Alcohols					
18	Methyl alcohol	26.4	244.8	0.11	65.2
19	Ethyl alcohol	17.0	169.1	0.10	73.5
20	*n*-Propyl alcohol	12.7	125.3	0.10	83.05
21	*n*-Butyl alcohol	7.8	97.6	0.08	86.3

(θ), the heat to be liberated by the capillary condensation of 1 mol. of liquid ($\Delta H'$), the amount of condensed liquid in 1 gram of rubber ($\theta/\Delta H'$), and the molecular polarization of the liquid (P). The molecular polarizations were obtained from the Transactions of the Faraday Society, September, 1934, containing articles on a general discussion of dipole moments.

A very regular hyperbolic functional relation between the molecular polarization of liquids and the amount of condensed liquid is evident in Fig. 3, and based on this relation the liquids are classified into three groups, that is, ordinary compound (curve A), halogen compound (curve B), and alcohol (curve C). In each group, the greater the polarity of the liquid, the less the amount of condensation.

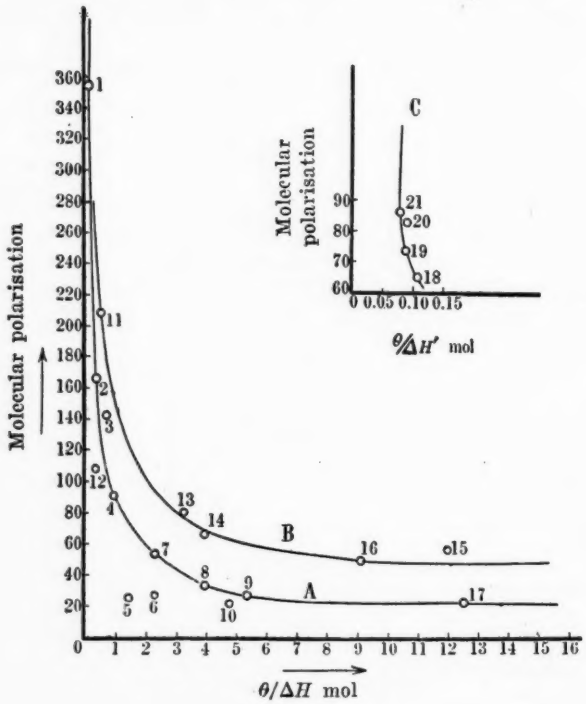

Figure 3

The amount of condensation of halogen compounds seems to be greater than that of ordinary compounds having the same order of molecular polarizations. The amount of condensation of alcohols is far smaller than of other liquids. Benzyl chloride, carbon tetrachloride, 1,4-dioxan, and cyclohexane deviate remarkably from the ordinary curves.

These results show that the polarity of natural crude rubber is very small. Halogen compounds react in some way with rubber. The heat of reaction is superposed on the heat of condensation, causing the separation of curves A and B. The most stable halogen compounds, such as carbon tetrachloride, show no deviation and behave as other ordinary compounds. The behavior of benzyl chloride is very peculiar. It has an intense effect on rubber, whereas its thermal effect is very small. The deviation of 1,4-dioxan and cyclohexane cannot be properly

explained. Alcohols may be affected by molecular association in the capillary spaces. A more detailed study of the behavior of alcohol in capillary spaces is being done in our laboratory to throw light on the minute structure of rubber films. The results will be reported in the near future. Thus, the observation of this thermal effect of vapors on rubber is a very interesting and effective method of studying the polar properties and minute structure of rubber.

Summary

The liberation of heat caused by immersing rubber films in vapors of various organic solvents having different molecular polarizations was measured quantitatively. The results show that natural crude rubber is a non-polar compound. Measurements of the thermal effect are shown to be of service in studying the polar properties and minute structure of rubber.

VI. POLAR PROPERTIES OF NATURAL AND SYNTHETIC RUBBER

In studying the polar properties of rubber, the thermal effects of vapors on rubber films were utilized, and the experiments were carried out in almost the same way as described in the previous paper. Test films were prepared by various methods from crude, purified, masticated, vulcanized, and chlorinated natural rubber, gutta-percha, and synthetic rubbers. The vapor of benzene was condensed on these films. Non-polar vapors are more easily condensed and liberate more heat from less polar films.

Preparation of Test Films

1. *Crude Rubber.*—As in the previous experiments, rubber films were prepared from the benzene extract of the acetone coagulum of latex.

2. *Purified Rubber.*—The film was prepared from whole rubber purified by the Pummerer method, as described in the previous paper (*J. Soc. Chem. Ind., Japan*, **38**, 506B (1935)).

3. *Irradiated (by Ultra-Violet Radiation) Purified Rubber.*—A purified rubber solution in a fused quartz flask was irradiated by a mercury lamp in the presence of air for 30 hours, and a film was prepared from this solution.

4. *Sol Rubber.*—The film was prepared from the ether extract of whole rubber.

5. *Masticated Rubber.*—Pale crepe sheet was masticated for 30 minutes by a mastication roll below 50° C., and used to prepare the film by being dissolved in benzene.

6. *Hot-Cured Rubber.*—Pale crepe sheet was masticated for 30 minutes; 100 grams of masticated rubber, 3 grams of sulfur, 1 gram of Tetrone A, 2 grams of stearic acid, and 5 grams of zinc oxide were mixed into it and the mixture was dissolved in benzene by shaking. Then the mixture was dried completely in a vacuum desiccator after dipping the test tube in this solution, and the tube was heated in a hot-air oven at 100° C. for 30 minutes.

7. *Cold-Cured Rubber.*—The test tube with the crude rubber film around it was immersed in 5% carbon disulfide solution of sulfur dichloride for 5 seconds, and then dried completely in a vacuum desiccator.

8. *Alkali-Reclaimed Rubber.*—The film was prepared from a benzene extract of alkali-reclaimed rubber, manufactured by Nippon Reclaimed Rubber Co.

9. *Chlorinated Rubber.*—A benzene solution of purified chlorinated rubber, manufactured by Hodogaya Soda Co., was used to make films.

10. *Gutta-Percha.*—The film was prepared from a benzene solution of gutta-percha purified by dissolving crude gutta-percha in benzene, filtering, coagulating

by adding alcohol to the filtrate, washing the coagulum with cold and hot water carefully, coagulating by acetone, and drying in a vacuum desiccator.

11. *Neoprene.*—The film was prepared from a benzene solution of Neoprene.

12. *Thiokol A.*—The ethylene tetrasulfide polymer was prepared from purified sodium tetrasulfide and dichloroethylene. The film was made from a carbon disulfide solution of the polymer.

13. *Synthetic Rubber No. 1969.*—The film was prepared from the carbon disulfide solution of a new synthetic rubber recently developed in our laboratory.

Results and Discussion

The quantities of heat liberated from the various films by absorption of benzene vapor are tabulated below.

TABLE III

Test Film	Heat Liberated, Cal./g. Film
Natural crude rubber	592.5
Sol rubber	420.0
Gutta-percha	329.2
Masticated rubber	325.3
Purified rubber	193.4
Hot-cured rubber	144.0
Chlorinated rubber	142.8
Cold-cured rubber	110.9
Irradiated (by ultra-violet rays) purified rubber	98.7
Alkali-reclaimed rubber	93.9
Neoprene	60.5
Synthetic rubber No. 1969	48.4
Thiokol A	43.3

Thus, natural crude rubber liberated the most heat in the films tested. Natural crude rubber is certainly a non-polar substance. Another experiment on the molecular polarization of crude rubber agreed with these results, as reported in the previous paper (*J. Soc. Chem. Ind., Japan*, **39**, 138B (1936)). As reported by Ostwald and Riedel (*Kolloid Z.*, **70**, 75 (1935)), mastication increases the molecular polarization of rubber. This may be caused by oxidation of the rubber in the process of mastication. The same results were obtained in our experiments. Purification, vulcanization, chlorination, and irradiation by ultra-violet light increase the molecular polarization. It is very interesting that alkali-reclaimed rubber shows greater polar properties than vulcanized rubber. Reclaimed rubber is assumed to contain much oxidized rubber vulcanizate formed by natural aging during the life of the rubber goods. This oxidation greatly increases molecular polarization. Neoprene and Thiokol A liberate very small amounts of heat. Synthetic rubber No. 1969 is a new oil-resisting rubber. The small quantities of heat liberated by these materials indicates that they have comparatively high polar and oil-resisting properties. The structure of these synthetic films should be investigated. Natural rubber and its derivatives are believed to have micellar structures, while synthetic rubber is a simple molecular polymer. The permeability of hydrogen gas and the water diffusion constant of synthetic films are far smaller than those of natural rubber (Sager, *India Rubber World*, **94**, 31 (1936); Taylor, Herrmann, and Kemp, *Ind. Eng. Chem.*, **28**, 1255 (1936)). These facts and the results in this paper indicate that synthetic films have almost no capillary spaces where the vapor can be condensed. This compactness and the high polar properties of the molecules seem to be the important factors governing the oil-resistance of rubber.

Summary

The thermal effects of benzene on various rubber films are correlated with the polar and oil-resisting properties of rubber. By means of quantitative experiments on these effects, natural crude rubber was proved to be a non-polar material; purification, vulcanization, mastication, irradiation by ultra-violet rays, and chlorination increase the polarity of rubber. Synthetic films show small thermal effects because of the high polar properties and the compactness of structure of the films.

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 13, No. 7, pages 110–118, July, 1937.]

Contributions to the Analysis of Rubber

II. The Qualitative Determination of the Serum Components of Raw Rubber and of Vulcanized Rubber

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Introduction

The use of latex in the rubber industry has been increasing to a considerable extent, and in many cases where formerly solutions of ordinary plantation rubber were used exclusively, *e. g.*, for impregnating fibres, spreading and adhering textiles, and manufacturing dipped goods, latex mixtures are now employed. Then again there is increasing interest in rubber prepared by evaporation or spraying of latex, especially for the production of powdered rubber. Consequently the time has come, as is evident from recent publications,[1] when it may be an important problem whether in the preparation of a rubber mixture it is best to use ordinary plantation rubber, latex, or, perhaps, evaporated latex. Now the peculiarity of a rubber mixture prepared from latex or from evaporated latex is its relatively high precentage of serum substances from the latex. In the first Communication on the present subject,[2] which dealt with the "Determination of the Water-Soluble Components of Rubber," a method was described for determining the serum substances in vulcanized rubber. In view of the fact that with technical rubber mixtures, and in the presence of zinc, calcium, and magnesium compounds, this method is complicated and tedious, the present experiments were carried out with an aim to developing a procedure for determining qualitatively the serum substances. A method of this kind must naturally be restricted to the identification of some substance which originates in the serum and not in the curvatives or other compounding ingredients.

Among the various substances which are present in latex serum, 1-methylinositol is one of the most important, and rubber mixtures prepared from latex or from evaporated latex contain a notable quantity of this substance. Consequently proof of the existence of 1-methylinositol in a mixture should be evidence of the presence of serum substances. The investigation to be described was therefore confined to the development of a characteristic reaction of 1-methylinositol.

Reactions of 1-Methylinositol

Scherer Reaction.—The old reaction of Scherer[3] was intended for inositol, and was described as follows.

"If inositol or a mixture containing inositol is evaporated with nitric acid almost to dryness on a platinum foil, if ammonium hydroxide and calcium chloride solution are then poured on the residue, and the solution is again evaporated cautiously to dryness, a bright rose-red coloration appears on the platinum. Other carbohydrates, including milk sugar, starch, cane sugar, and glucose, give absolutely no color by this treatment. The reaction is not only characteristic but sensitive. One-half milligram of inositol gives an intense color."

Whitby, Dolid, and Yorston have reported[4] that, by extraction of first latex plantation rubber with glacial acetic acid, 1-methylinositol can be identified easily by the Scherer reaction.

In the Netherlands Government Rubber Institute at Delft, analyses of 1-methylinositol[5] and inositol[6] were carried out in the following way.

The aqueous solution containing 1 mg. of the substance under investigation was evaporated on the cover of a platinum crucible, 0.4 cc. of nitric acid (d. 1.4) was added to the residue, the mixture was evaporated almost to dryness, the residue was treated with 0.4 cc. of 25 per cent ammonium hydroxide and 0.3 cc. of 1 per cent calcium chloride solution, and the mixture was evaporated cautiously to dryness, first on a water bath and then over a micro-burner. Under these conditions, no rose-red color was evident. On the contrary, this color was obtained when the nitric acid was evaporated completely on the water bath and, after cautious evaporation of the ammonia and calcium chloride solution, the residue was heated at 140° C. In this case, a red color appeared after a few minutes, and it gradually increased in intensity on further heating. With 1-methylinositol, heating for 1 hour gave a red-brown stain; with inositol the entire surface of the platinum became rose-red. The reaction is not then the same for 1-methylinositol and for inositol, but in either case it is very sensitive when carried out in this way, *e. g.*, after heating for 1 hour, 0.1 mg. of 1-methylinositol and 0.5 mg. of inositol still give a pale reddish coloration.

The same results were obtained when, after evaporation on a water bath, the residue was heated further very cautiously with a micro-burner.

Further experiments were carried out in an effort to apply the reaction to the water-soluble components of evaporated latex. A 152-mg. sample of extract, obtained from 2 grams of rubber, was dissolved in 5 cc. of water, and various quantities of this solution were tested.

Table I summarizes the results of heating for 1 hour at 140° C., and of heating with a micro-burner.

TABLE I

SCHERER REACTION WITH WATER-SOLUBLE COMPONENTS OF RUBBER

Weight of Rubber (Grams)	Weight of Extract (Mg.)	140° C.	Micro-burner
0.5	38	No reaction	No reaction
0.25	19	No reaction	No reaction
0.10	7.6	No reaction	No reaction
0.05	3.8	Slight reaction	Slight reaction
0.025	1.9	Slight reaction	Slight reaction
0.010	0.76	No reaction	No reaction

The results in Table I show that a slight reaction is obtained only with a small quantity of extract. With larger quantities of extract, in other words with more 1-methylinositol, there is no color reaction.

Similar results were obtained when the reaction was carried out with water-soluble components obtained by water extraction on a water bath, and with an extract obtained by boiling with glacial acetic acid for one-half hour.

With water-soluble substances from plantation rubber, obtained by the new method (cf. the first Communication)[2] and by extraction with glacial acetic acid, 5 mg. of extract gave a reddish color, whereas 10 mg. and 20 mg. gave no color.

On the basis of these observations, it may be concluded that the Scherer reaction is unsuitable as a qualitative reaction for distinguishing first-latex plantation rubber from evaporated latex rubber.

Schoorl Reaction.—On enquiry at the Schoorl Institute of Utrecht, unpublished information on a reaction of 1-methylinositol was obtained from Professor Schoorl.[7] This reaction is based on the cleavage of the methoxy group and oxidation to formaldehyde. The procedure is carried out in the following manner.

Heat 50 mg. of 1-methylinositol with 0.5 cc. of concentrated sulfuric acid for one-half hour, aiding solution by rubbing with a glass rod; cool, dilute with 5 cc. of water, add 0.5 cc. of 5 per cent potassium permanganate, let stand for one-half hour, decolorize with 1 cc. of 10 per cent oxalic acid; to 1 cc. of solution add an equal volume of Schiff reagent.[8] On standing several hours, a violet coloration appears. No color is obtained in an acid solution of this kind with other aldehydes

In addition to the reaction with Schiff reagent, the formaldehyde reaction of Leach was also investigated. The procedure was to mix 5 cc. of liquid with 7 cc. of 25 per cent hydrochloric acid (containing 0.2 cc. of 10 per cent ferric chloride per 100 cc. of hydrochloric acid) and 2 cc. of fresh milk, and boil for 15 seconds. If formaldehyde is present, a violet coloration appears. The results are summarized in Table II.

TABLE II

SCHOORL REACTION OF 1-METHYLINOSITOL AND LEACH REACTION OF FORMALDEHYDE

1-Methyl-inositol (Mg.)	Leach Reaction	Schiff Reagent
50	++	+++
20	+	+++
10	0	++
5	0	0

Here 0 means negative or very weak, + means weak, ++ means medium, +++ means strong.

The data in Table II show that with Schiff reagent the reaction is more sensitive than is the Leach reaction. However, even with Schiff reagent the sensitivity is not great, and experiments were carried out in an attempt to increase it. A complete description of the results obtained with 1-methylinositol and serum substances would require so much space that only the most important results will be mentioned.

1. The sensitivity of the reaction is considerably increased if the substance dissolved in water is oxidized by sulfuric acid and potassium permanganate; heating with sulfuric acid on a water bath thereby being avoided. To assure an excess of potassium permanganate during the oxidation, over 0.5 cc. of a 5 per cent solution is necessary, *e. g.*, 50 mg. of 1-methylinositol require 2 cc. of solution.

2. The sensitivity diminishes with increase in the quantity of potassium permanganate, and with increase in the time of oxidation.

3. The sensitivity is greatest when the aqueous solution is oxidized without sulfuric acid, and is then decolorized by sulfuric acid and oxalic acid. In view of the small quantities of 1-methylinositol present in ordinary plantation rubber, such sensitivity is not desirable.

4. The small quantities of 1-methylinositol present in ordinary plantation rubber give a negative reaction if the following modified procedure is followed.

Dissolve the water-soluble substances from raw rubber in a mixture of 5 cc. of water and 0.5 cc. of concentrated sulfuric acid, to every 50 mg. of extract add 0.5 cc. of 5 per cent potassium permanganate (minimum 0.5 cc., maximum 2 cc.), let stand for one-half hour, decolorize with 1 cc. of 10 per cent oxalic acid, mix 1–2 cc. of the decolorized solution with an equal volume of Schiff reagent,[10] and examine the color after one-half hour. If the reaction is strong, a blue-violet color is evident

after a few minutes. The remaining part of the oxidized solution can be used for the Leach reaction.

The sensitivity of this reaction is less than with Schiff reagent.

The modified form of the Schoorl method was used for analyzing the following three components of raw rubber

(*a*) the water-soluble components of the acetone extract,

(*b*) the water-soluble components in rubber, previously extracted with acetone, determined by the recently described steam-distillation method,[2]

(*c*) the water-soluble components, as determined by the old method (simple extraction with water).[2]

TABLE III

THE 1-METHYLINOSITOL REACTION IN THE WATER-SOLUBLE PORTION OF THE ACETONE EXTRACT OF RAW RUBBER

Rubber		Extract (Percentage)	Oxidation for 30 Minutes: Leach Reaction	Oxidation for 30 Minutes: Schiff Reagent	Oxidation for 5 Minutes: Leach Reaction	Oxidation for 5 Minutes: Schiff Reagent
First latex crepe	364	0.3	0	0	0	++
	367	0.3	0	0	0	++
	372	0.2	0	0	0	++
	357	0.3	0	0	0	++
	365	0.2	0	0	0	0
	372	0.2	0	0	0	++
Hopkinson rubber		0.8	+	++		
Rubber powder		2.3	+++	+++		
Rubber powder		2.4	+++	+++		
Evaporated latex		1.3	+++	+++		
Evaporated latex		1.8	+++	+++		
Evaporated latex		1.7	+++	+++		
Evaporated concentrated latex		0.7	+	++		
Evaporated concentrated latex		1.0	++	+++		
Evaporated concentrated latex		0.5	0	+		

TABLE IV

THE 1-METHYLINOSITOL REACTION IN THE WATER-SOLUBLE COMPONENTS OF RAW RUBBER, AS DETERMINED BY THE STEAM-DISTILLATION METHOD AND BY THE OLD SIMPLE EXTRACTION METHOD

Rubber	New Methods: Extract (Percentage)	New Methods: Leach	New Methods: Schiff	Old Methods: Extract (Percentage)	Old Methods: Leach	Old Methods: Schiff
First Latex Crepe 364	0.8	0	0	0.2	0	0
First Latex Crepe 367	0.7	0	0	0.2	0	0
First Latex Crepe 372	0.7	0	0	0.1	0	0
First Latex Crepe 357	0.9	0	0	0.3	0	0
First Latex Crepe 365	0.9	0	0	0.2	0	0
First Latex Crepe 375	0.8	0	0	0.2	0	0
Hopkinson rubber	4.0	++	+++	1.4	+	++
Rubber powder	5.7	+++	+++	4.4	+++	+++
Rubber powder	5.5	+++	+++	4.0	+++	+++
Evaporated latex	6.3	+++	+++	2.9	+++	+++
Evaporated latex	9.9	+++	+++	7.9	+++	+++
Evaporated latex	8.8	+++	+++	6.8	+++	+++
Evaporated concentrated latex	2.2	+	++	0.5	0	0
Evaporated concentrated latex	3.0	++	+++	1.3	+	++
Evaporated concentrated latex	1.1	0	+	0.1	0	0

The results obtained with the water-soluble components of the acetone extract of various rubbers are summarized in Table III. To show the influence of the time of oxidation, tests of ordinary plantation rubbers oxidized for only 5 minutes are included in the tabulated data.

It is evident from the data in Table III that considerable quantities of 1-methylinositol are present in the acetone extracts of different types of rubber which have been prepared by evaporation of latex. The results of the tests after oxidation for 5 minutes show that small quantities of 1-methylinositol are present also in the acetone extract of ordinary plantation rubber. However, these quantities are so small that after oxidation for 30 minutes the reactions were negative in all cases.

The results which were obtained with the water-soluble components, determined both by the new steam-distillation method and the old method, are summarized in Table IV. The new method was carried out with acetone-extracted rubber.

The results in Table IV show that considerable quantities of 1-methylinositol are still present in rubber obtained by evaporation of latex, even after the rubber has been extracted with acetone. No 1-methylinositol was detected in the serum components or ordinary plantation rubber. The water-soluble substances from evaporated latex rubber, obtained by the old simple extraction method, gave a strong reaction of 1-methylinositol, whereas those from evaporated concentrated latex rubber gave a negative reaction.

Examination of Rubber Mixtures and of Vulcanized Rubber

Samples of raw rubber, including first latex crepe, first latex sheet, evaporated latex, Hopkinson rubber, and rubber powder were compounded in the formula: rubber 100, sulfur 5, diphenylguanidine 1, zinc oxide 3, and were vulcanized for 20 minutes at 147° C. The water-soluble components were separated by the steam-distillation method. Since, however, zinc oxide is dissolved during the heating with acetic acid, the water-soluble substances were dissolved again in water after evaporation to dryness, the zinc compounds were precipitated with hydrogen sulfide, were removed by filtration, and the filtrate was evaporated and dried at 100° C. The extract obtained in this way was then examined. The results are summarized in Table V.

It is evident from Table V that the same results were obtained with a particular

TABLE V

THE 1-METHYLINOSITOL REACTION IN THE WATER-SOLUBLE COMPONENTS OF RUBBER MIXTURES AND VULCANIZED RUBBER

Sample	Extract (Percentage)	Formaldehyde Reaction	
		Leach	Schiff
First latex crepe, raw	0.8	0	0
First latex crepe, vulcanized 20 min.	1.0	0	0
First latex sheet, raw	0.8	0	0
First latex sheet, vulcanized 20 min.	0.9	0	0
Evaporated latex, raw	5.8	++	+++
Evaporated latex, vulcanized 10 min.	5.6	++	+++
Evaporated latex, vulcanized 20 min.	5.4	++	+++
Hopkinson rubber, raw	5.1	++	+++
Hopkinson rubber, vulcanized 10 min.	5.2	++	+++
Hopkinson rubber, vulcanized 20 min.	5.0	+	+++
Rubber powder, raw	5.6	++	+++
Rubber powder, vulcanized 10 min.	5.9	++	+++
Rubber powder, vulcanized 20 min.	5.5	+	+++

rubber before and after vulcanization. There were distinct differences between rubber mixtures prepared from ordinary plantation rubber and the corresponding mixtures prepared from normal latex or concentrated latex.

An investigation was then made of the influence of fillers on the 1-methylinositol reaction. Obviously in this study the samples were previously extracted with acetone, because the presence of accelerators and other ingredients leads to errors.

Influence of Glue

It was proved by means of vulcanized rubber mixtures prepared from ordinary plantation rubber, and containing 9 per cent of glue, that the glue present in the water-soluble substances has no significant influence on the l-methylinositol reaction.

Influence of Zinc, Calcium, and Magnesium Acetates

In determining water-soluble substances by the steam-distillation method, any zinc, calcium, and magnesium compounds which may be present in the rubber mixtures are transformed into their acetates. In the earlier communication[2] it was shown that these acetates can be eliminated by changing the method of procedure.

Mixtures of first latex crepe and of evaporated latex of the composition: rubber 100, sulfur 5, diphenylguanidine 1, zinc oxide 3, calcium oxide 5, magnesium oxide 5, were vulcanized for 20 minutes at 147° C. Zinc, calcium, and magnesium were eliminated in succession from the water-soluble substances, and the residues were tested for the 1-methylinositol reaction. The results are tabulated in Table VI.

TABLE VI

INFLUENCE OF ZINC, CALCIUM, AND MAGNESIUM ACETATES

	First Latex Crepe Mixture			Evaporated Latex Mixture		
Sample	Extract (Percentage)	Leach	Schiff	Extract (Percentage)	Leach	Schiff
Zinc, calcium, and magnesium absent	30.5	0	0	33.5	+	+++
Zinc eliminated	23.1	0	0	27.0	++	+++
Zinc and calcium eliminated	9.9	0	0	12.0	++	+++
Zinc, calcium, and magnesium eliminated	1.7	0	0	4.0	++	+++

The data in Table VI show that the presence of zinc, calcium, and magnesium acetates has no influence on the 1-methylinositol reaction.

Influence of Textiles

To ascertain the influence of textiles, the water-soluble components of canvas and of two transmission belts were examined. Two grams of canvas and 5 grams each of the belt samples were used. The water-soluble substances were determined both by the older simple water-extraction method and by the new steam-distillation method. Belt A was made with ordinary plantation rubber, belt B with a latex mixture. The results of the tests are summarized in Table VII.

The results in Table VII show that water-soluble substances in textiles give a positive reaction, and therefore would have a disturbing influence on a test for 1-methylinositol in rubber.

It was shown in the first communication[2] that the content of water-soluble components is reduced by treatment with lead acetate.

TABLE VII

INFLUENCE OF TEXTILES ON THE 1-METHYLINOSITOL REACTION

Sample	The Old Method			Steam Distillation Method		
	Extract (Percentage)	Leach	Schiff	Extract (Percentage)	Leach	Schiff
Canvas	2.4	++	+++	2.8	++	+++
Belt A	2.2	++	+++	8.8	+	++
Belt B	3.6	++	+++	17.1	++	+++

Table VIII gives the results obtained after treatment with lead acetate.

TABLE VIII

INFLUENCE OF TEXTILES ON THE 1-METHYLINOSITOL REACTION AFTER TREATMENT OF THE WATER-SOLUBLE SUBSTANCES WITH LEAD ACETATE

Sample	The Old Method			Steam Distillation Method		
	Extract (Percentage)	Leach	Schiff	Extract (Percentage)	Leach	Schiff
Canvas	1.8	0	0	2.5	0	0
Belt A	1.5	0	0	1.8	0	0
Belt B	2.6	++	+++	12.0	++	+++

The results in this table show that after treatment with lead acetate, the reaction was positive only for the sample made from evaporated latex. Accordingly lead acetate removes water-soluble substances which on oxidation give rise to formaldehyde. It was proved that these substances are eliminated during the precipitation of excess lead acetate by hydrogen sulfide. When the excess of lead acetate was not removed, the reaction was positive, in spite of the fact that lead acetate itself has no influence on the reaction.

In this exceptional case, both methods in Table VIII gave the same results with respect to the 1-methylinositol reaction; however, this is because of the low degree of vulcanization of sample B.

TABLE IX

QUALITATIVE TESTS OF THE SERUM SUBSTANCES IN VULCANIZED RUBBER PRODUCTS

Rubber Product	Formaldehyde Reaction	
	Leach	Schiff
Red table cover (from latex)	++	+++
Gray table cover (from latex)	++	+++
Transparent table cover (from latex)	++	+++
Gloves (from rubber solution)	0	0
Gloves (anode process)	0	0
Gloves (from latex)	+	+++
Thread (square)	0	0
Thread (square)	0	0
Thread (square)	0	0
Sponge rubber (from rubber powder)	+++	+++
Inner soles	++	+++
Impregnated cord	++	+++
Sheet with fabric	++	+++

Since the reaction is so very sensitive, complete extraction is perhaps not necessary.

In this connection the attempt was made to learn whether serum substances are

extracted to a sufficient extent by glacial acetic acid. It was found that after boiling for 1 hour only a portion of the serum substances was extracted, and that the higher the degree of cure of the rubber mixture, the smaller the quantity extracted. After boiling for 1 hour and evaporation of the acetic acid, the quantity of extract then obtained was sufficient for a good reaction in the case of vulcanizates prepared from evaporated latex. In a few cases, however, negative reactions were obtained with the acetic acid extracts, although the reactions were very distinct with the corresponding extracts by the steam-distillation method.

Accordingly when the reaction of the acetic acid extract is negative, a test of the extract by the steam-distillation method should also be made.

In conclusion, the results of some tests of various types of vulcanized rubber products are itemized in Table IX.

The results tabulated in Table IX show the differences which are evident between rubber goods prepared from ordinary plantation rubber, from latex and from evaporated latex.

Résumé

It has been demonstrated that the old reaction of Scherer[3] is not adapted to the qualitative determination of serum substances. On the contrary, by suitable modification of an unpublished reaction of Schoorl,[7] it was found possible to identify 1-methylinositol in the water-soluble components of raw rubber and vulcanized rubber. The reaction is carried out under controlled conditions of sensitivity so that the color reaction of 1-methylinositol is positive only with the water-soluble substances from evaporated latex (whole latex rubber), and is correspondingly negative with the serum substances from first-latex crepe or sheet. In this way it becomes possible to decide whether a rubber mixture has been prepared from ordinary plantation rubber or from latex or evaporated latex.

The *procedure* is carried out in the following manner.

Heat 2 grams of acetone-extracted rubber with 80 cc. of xylene and 5 cc. of glacial acetic acid on an oil bath until the rubber is dissolved, after complete solution add 5 cc. of glacial AcOH and 10 cc. of water, heat for 2 hours more on the oil bath at 110° C., eliminate the xylene by steam distillation, filter the residual aqueous solution, evaporate the filtrate, dissolve the residue in 5 cc. of 20 per cent sulfuric acid, add 0.5 cc. of 5 per cent potassium permanganate (if the latter is consumed after 5 minutes add a little more, but at the most not over 2 cc.), let stand for one-half hour, decolorize the solution with 1 cc. of 10 per cent oxalic acid solution, mix 2 cc. of the resulting solution with 2 cc. of Schiff reagent,[10] let stand for one-half hour and judge the color. If serum substances are present, a blue-violet coloration appears. The remaining portion of the oxidized solution can be tested for formaldehyde by the method of Leach.[9]

Rubber Mixtures Containing Textiles.—If the rubber sample under investigation contains a textile, the procedure must be modified. In this case dissolve the residue from the steam-distillation method[2] in 50 cc. of water, add 3 cc. of 10 per cent lead acetate solution, let stand for one-half hour, filter, precipitate the excess lead acetate by hydrogen sulfide, filter, evaporate the filtrate, and treat the residue as already described.

When the rubber content of the sample is small, it is preferable to use more than 2 grams, not, however, more than 4 grams.

In many cases the extract obtained by boiling glacial acetic acid is sufficient for the 1-methylinositol reaction. After boiling for 1 hour with 25 to 50 cc. of glacial acetic acid, filter, evaporate the acetic acid on a water bath, and then test the residue as before for the presence of serum substances. If the reaction is negative,

it is desirable to repeat the test with the extract obtained by the steam-distillation method.[2]

The author extends his sincere thanks to A. van Rossem, Director of the Institute, for his helpful collaboration in this investigation.

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[5] The Research Association of British Rubber Manufacturers (Croydon) was kind enough to place this substance at the disposal of the author.

[6] Poulenc Frères, Paris, France.

[7] Private communication. The heartiest thanks are due Professor Schoorl for his collaboration in this way.

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[9] *Ann. Rept. Man. State Board of Health*, **1899**, 558.

[10] Two hundred mg. of crystallized fuchsin dissolved in 20 cc. of fresh saturated sulfur dioxide solution, diluted to 200 cc. of water after 24 hours.

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The Evolution of Heat during Vulcanization

S. Oberto

Though already the subject of numerous investigations, the thermochemistry of vulcanization seems still to be an incomplete chapter in the physical chemistry of rubber. As a matter of fact precise determinations of the heat liberated in the reaction of rubber with sulfur are still lacking, particularly for ordinary vulcanizing temperatures (120–140° C.) and for proportions of sulfur from 1 to 4 per cent, based on the rubber.

The first data to appear on the subject, published by several authors, were based on the difference between the heat of combustion of an unvulcanized rubber mixture and that of the same mixture after vulcanization. Weber,[1] for example, attributes to the heat of formation of sulfur chloride the readiness with which the latter vulcanizes rubber. Blake[2] vulcanized rubber mixtures containing various proportions of sulfur, and found that the heats of combustion varied directly with the proportion of sulfur above 4 per cent, but that the values were insignificant below 4 per cent sulfur. Hada, Fukaya, and Nakajima[3] obtained results which indicate that there is an endothermic reaction around 1 per cent of combined sulfur. Jessup and Cummings[4] concluded from their measurements that the heat of vulcanization is a linear function of the combined sulfur, but their measurements for 2 and 6 per cent sulfur are somewhat uncertain.

A method which is based on the determination of heats of combustion is unsuitable for the end in view when differences of only a few calories in thermal balances of the order of 10,000 calories are involved. The most reliable and at the same time the most extensive data have been obtained by experimental methods based on measurements of the elevation of temperature within a mass of rubber during vulcanization, or by calorimetric measurements. Seidl[5] measured the increase in temperature within a rubber mixture accelerated by litharge over that of the surrounding oil bath, and concluded that the heat liberated is to a great extent attributable to a reaction between litharge and hydrogen sulfide. Buizov[6] and Kirchhof and Wagner[7] observed considerable increases in temperature during the vulcanization of rubber-sulfur mixtures. In experiments with high percentages of sulfur, Perks[8] calls attention to the importance of the heat of fusion of sulfur absorbed during the heating, and he found notable increases in temperature. Williams and Beaver[9] devised an experimental apparatus by means of which they measured with a thermocouple, sensitive to 0.5° C., the temperature at the center of a cylinder of rubber during its vulcanization in a constant-temperature bath; then in a calorimeter in which it was possible to produce known quantities of heat electrically. A temperature of 175° C. was used, and heats of vulcanization of approximately 20 calories per gram of rubber mixture were found.

Boström[10] studied vulcanization with sulfur chloride in a calorimeter and obtained a value of 3 calories per gram of rubber. Kimishima[11] utilized the method of Williams and Beaver so that he could take into account the different rates of vulcanization with different accelerators. He too used a high temperature, *viz.*, 165° C., and merely determined the maximum temperature in the middle of the rubber above the temperature of the surrounding bath.

Toyabe[12] carried out experiments at 155–170° C., and measured both the maximum temperatures and the times necessary to reach these maxima. Similarly Hada and Nakajima[13] experimented at 160° C. Blake[14] employed a temperature of vulcanization of 184.4° C., and attempted to obtain an approximate value of the number of calories evolved in the combination of rubber with sulfur. He obtained a value of 10 for 4 per cent of sulfur; he was therefore the first to show that there are positive thermal balances for 1 per cent of sulfur. Horie and Morikawa[15] vulcanized rubber at 160°, and determined only the maximum temperatures attained. Daynes[16] made a theoretical study of the increase in temperature during vulcanization of ebonite, basing his study on the effects of the heat of vulcanization. McPherson and Bekkedahl[17] used a calorimetric method and a temperature of 165° C.

A study of the literature leads then to the conclusion that all authors who have investigated the increases of temperature during vulcanization have utilized temperatures above 150° C. Under these conditions highly accelerated rubber mixtures overcure rapidly, and if an experiment is continued beyond a brief time, thermal balances of reactions which do not take place in actual vulcanization must be taken into account. On the other hand a short experiment is impracticable because of the poor thermal conductivity of rubber, which retards an early attainment of a temperature level. Furthermore with some rubber mixtures, vulcanization at one temperature cannot be compared, on a basis of the physical properties of the vulcanizates, with vulcanization at some other temperature; and this fact makes it equally inopportune to employ very high temperatures for determining heats of vulcanization.

A study of the literature also reveals the fact that the thermal balance, expressed in calories, has been calculated by only a few investigators, and in these cases with none too great precision. In the present work, the attempt was made to develop a method which, in contrast to earlier work, would give with satisfactory approximation the heat evolved during the reaction of rubber with sulfur at vulcanizing temperatures of only 110° C., and for rubber mixtures containing more usual percentages of sulfur, *i. e.*, around 3 per cent or even lower.

Method of Calculating the Heat of Vulcanization

The heat of vulcanization of a rubber mixture can be calculated with good approximation by working under the best and most accurately controlled conditions, *e. g.*, by a study of vulcanization of a sheet of rubber. The problem will first be treated theoretically.

In an indefinitely large sheet of thickness, l, the faces of which are maintained at a strictly constant temperature, T, let q be the small calories of heat per unit volume evolved per second. Let λ be the thermal conductivity, c the specific heat, and ρ the density of the sample in sheet form. Let us now consider successive equal intervals Δt of time.

The heat evolved, q, is in general constant during such an interval of time. The process in question is therefore not isothermic, nor is it adiabatic, since the faces of the sheet are supplied with an external source of heat, either positive or negative, at temperature T. The process can, however, be resolved into a succession of isothermal and adiabatic processes, by dividing q for each sufficiently small interval of time Δt into two parts, q_1 for the isothermal process and q_2 for the adiabatic process. Let T' be the temperature of the middle section of a sheet of rubber at the beginning of any time interval; at the end of this interval the temperature is $T' + \Delta T'$, with $\Delta T'$ relatively small compared with $T' - T$. It may be assumed that, in an approximate way, there is for each ΔT a loss of heat from the rubber through its two surfaces,

as if the rubber sheet were in equilibrium with the middle section at temperature T'; the calculation then becomes:

$$q_1 = \frac{8\lambda(T' - T)}{l^2}$$

During the interval the temperature of the middle section of the sheet of rubber changes by the amount $\Delta T'$. From what has been said, it may be assumed that all of the sheet has changed in temperature by $\Delta T'$.

Consequently

$$q_2 = c\rho \frac{\Delta T}{\Delta T'}$$

It should be noted that q_1 and q_2, as well as q, refer to unit volume and unit time. At the end of n time intervals, the quantity of heat Q evolved up to this point by unit volume is represented by the equation:

$$\begin{aligned} Q &= \sum_o^n (q_1 + q_2)\,\Delta t \\ &= \frac{8\lambda}{l^2} \sum_o^n (T' - T)\,\Delta t + c\rho \sum_o^n (\Delta T') \\ &= \frac{8\lambda}{l^2} \sum_o^n (T' - T)\,\Delta t = c\rho(T'_n - T'_o) \end{aligned}$$

Dividing by $c\rho$, and calling $\frac{\lambda}{c\rho} = a^2$ the thermometric conductivity, the temperature Θ of the rubber sheet in the total absence of heat losses is obtained:

$$\Theta = \frac{8a^2}{l^2} \sum_o^n (T' - T)\,\Delta i + (T'_n - T'_o)$$

Since Θ multiplied by $c\rho$ gives Q, the expression for Θ is more adaptable to calculation; it is also simpler to determine a^2 than λ experimentally. If the rubber sheet is composed of a mixture, and T is the temperature of vulcanization, a method of calculating the heat evolved during vulcanization is available, not only as a total thermal balance, represented by the value of Q when n is sufficiently great, but also in the successive steps of vulcanization. There is thus obtained a diagram giving the heat evolved by unit volume as a function of the time of vulcanization, which may be compared with known diagrams of tensile strength, combined sulfur, etc., as functions of the time of vulcanization.

For experimental and calculated results to be in agreement, it is necessary that q be the same at each instant at every point in the rubber. Vulcanization will then proceed simultaneously in every part of the rubber mixture, and the temperature will be practically uniform throughout. The thickness of the rubber sheet is therefore reduced to the point where the time of the preliminary heating necessary to raise it, say, to within 1 degree of the vulcanizing temperature, is negligible in comparison with the total time of heating, *e. g.*, of the order of magnitude of 5 minutes in comparison with a total time of 1 hour. Furthermore the heat of vulcanization which raises the temperature of the middle section of the rubber sheet does not in turn bring about any appreciable irregularity in the state of vulcanization.

A maximum value of $T' - T$ of 1° C. can be assumed unreservedly, and this amounts to a maximum difference of 10 per cent in the state of vulcanization between the middle section and the surfaces of the rubber sheet. The thickness of the sheet was less than 1 centimeter.

All earlier experimenters have operated at relatively high vulcanizing temperatures and with relatively thick samples of rubber, and therefore have found excess temperatures of several degrees within the mass of rubber. Their experimental conditions were somewhat less rigorously chosen, and were less well adapted to calculation.

Experimental Apparatus and Technic

On the basis of the foregoing theoretical discussion, and as a result of preliminary experiments, the apparatus and technic finally developed for studying heats of vulcanization were as described below.

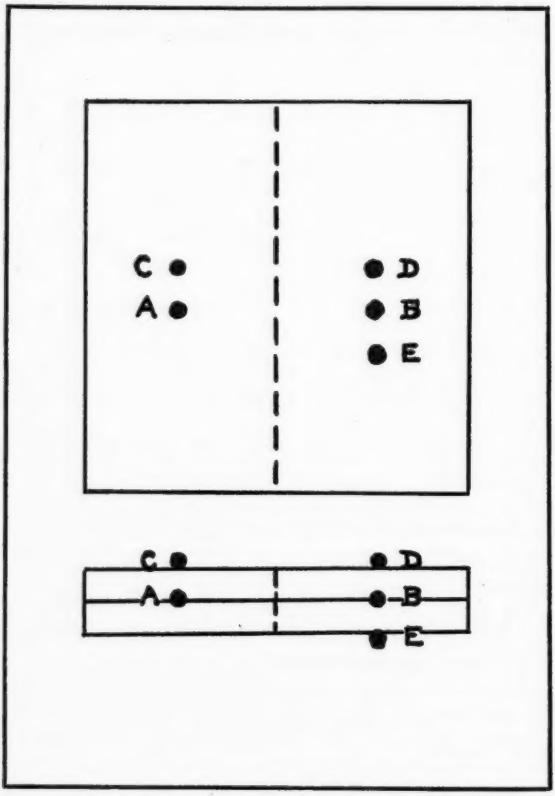

Figure 1—Positions of the Thermoelectric Couples

Two half-size sheets of rubber mixture, accurately weighed and measured, were placed side by side in a square mold 25 cm. × 25 cm. × 0.8 cm. thick. One of the half-size sheets was the sample mixture, the heat of vulcanization of which was to be measured; the other half-sheet was an identical mixture except that it contained no sulfur. However, when it was desired to study the parallel or secondary reactions, *e. g.*, between accelerators and zinc oxide or between different accelerators, the two half-size sheets naturally differed in this respect rather than by the presence and

absence of sulfur. In every case the surface temperature of the control half-size sheet was considered to be T.

Differences in temperature between points A and B (see Fig. 1) in the middle sections of the sheets were measured by a differential thermoelectric couple, multiple where necessary. The slight thickness of the rubber sheets compared to their lateral dimensions made it certain that the disturbing effect of the edges of the mold did not influence in any appreciable way the temperatures at points A and B. The couples were of constantan-copper wire 0.3 mm. in diameter, and these wires were laid zigzag in order to be able to follow the local movements of the rubber during pressing, and to diminish any chance perturbations arising from the high thermal conductivity of the metal. The copper in particular was thoroughly insulated from the rubber by extremely thin bits of mica, to prevent the formation of copper sulfide during vulcanization.

The differential couple was connected with a galvanometer, by means of which the increases in temperature could be registered photographically. In the actual experiments, a sensitivity on the diagram of 0.02° C. per millimeter of displacement was obtained, and even 0.01° C. could be detected.

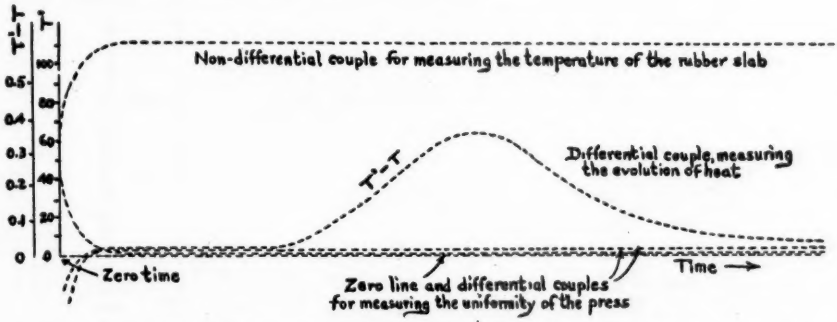
Non-differential couple for measuring the temperature of the rubber slab
Differential couple, measuring the evolution of heat
T'-T
Zero time
Zero line and differential couples for measuring the uniformity of the press
Time

Figure 2—Typical Experimental Diagram of the Temperature Trend in a Rubber Slab

For greater precision of technic, another differential thermoelectric couple was placed on one surface of the slabs to measure the difference in temperature between points C and D; still another couple, likewise of high sensitivity, measured the difference in temperature between points D and E. Finally a non-differential thermocouple measured the vulcanizing temperature T' at the center of the sheets, which differed but little from temperature T. All thermocouples were connected with the same galvanometer (the non-differential thermocouple through a high resistance), and were put successively in circuit with an automatic recording apparatus. The quick action of the galvanometer made it possible to register the readings of all the thermocouples each minute; the complete diagram gave a record of the entire series of measurements in an experiment, with every variation in the temperature of the rubber slab.

The rubber was vulcanized between plates in a press in which there was perfect circulation of live steam. Under these conditions, slight differences were observed between the temperatures of points C, D, and E, of the order of a 0.02° C. (the differences were a little greater at 110° C.). These differences were considered to have no significant influence on the results. Even a considerable variation in the time-temperature relation of the press, if the effect is the same on the two surfaces of the rubber, has no influence on the differential measurement at points A and B, except

in cases where the two half-slabs differ greatly in their loadings, which make their thermal conductivities differ.

After three or four minutes, during which vulcanization commences, the thermocouples are connected to the galvanometer, care is taken to make certain that everything is in adjustment, and the experiment proceeds. The calculations are made on the photographic diagram, an example of which is shown in Fig. 2; Δt intervals from 5 to 10 minutes, and even 2 minutes in exceptional cases where the liberation of heat is extremely rapid, are chosen.

Experimental Results

The experimental values obtained are in general rather significant, despite the fact that the errors in measuring the heats of vulcanization were of the order of 0.1 small calorie per cc. of rubber mixture.

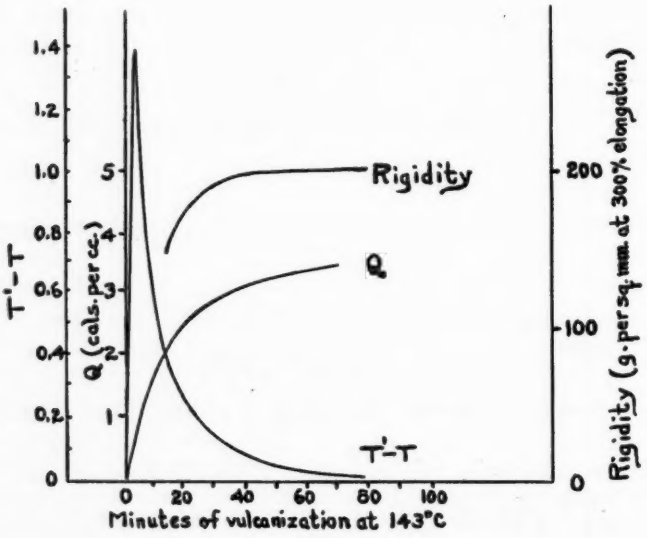

Figure 3—Mixture Containing Tetramethylthiuram Disulfide and No Sulfur

A first series of tests naturally was carried out with unaccelerated mixtures, of the composition: rubber 100, sulfur 8, with various rubbers, none of which was purified or deresinated in any way. Evolution of heat commenced immediately, passed through a slight maximum, and subsided gradually. At the vulcanizing temperature of 143° C., the maximum evolution was reached after 1 hour, and after 4 hours evolution of heat was only one-half of the maximum value. Since parallel determinations of combined sulfur were not made, partial thermal balances, which varied around 10 calories per cc. for 3 hours at 143° C., are of relatively little significance.

A second series of tests was devoted to an examination of inorganic accelerators. Probably secondary reactions in vulcanization accelerated with inorganic accelerators, and with a sulfur content of about 5 per cent, account for thermal balances even greater than 15 calories per cc. On the contrary, acceleration with

organic accelerators, with sulfur contents about 3 per cent, gives heats of vulcanization of approximately 4 calories per cc.

Let us examine in detail the heat which is evolved during the vulcanization of three highly accelerated mixtures, containing low percentages of sulfur, and showing notable plateau effects, *i. e.*, having the same mechanical properties over a range of states of vulcanization.

These three examples serve to show how the vulcanization of a rubber mixture may be examined from the thermochemical point of view. They are to a certain extent related to the experiments of Blake on the heats of reaction with various percentages of combined sulfur. According to Blake, initial combination of rubber and sulfur, *i. e.*, for the first few per cent of combined sulfur, is followed by com-

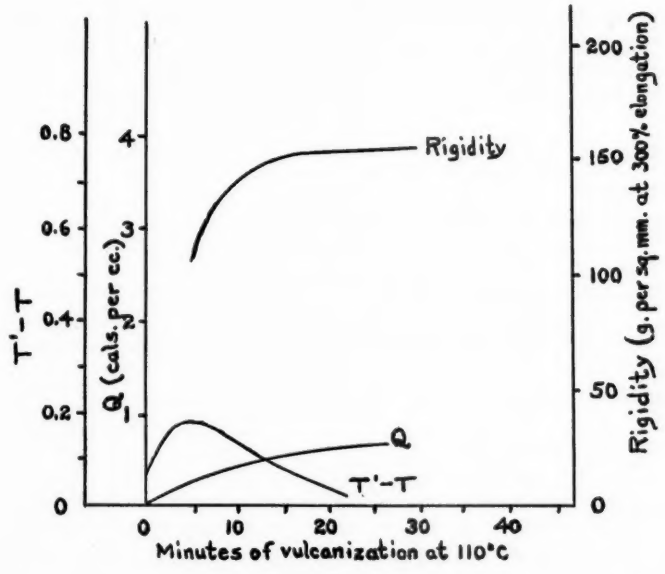

Figure 4—Mixture Containing 0.8 Per Cent Sulfur and Piperidinium Pentamethylenedithiocarbamate

bination under conditions of greater heat tone, and this latter state is responsible for the poorer aging of vulcanizates containing higher percentages of combined sulfur.

For each of the mixtures examined, the diagrams show, as functions of the time of vulcanization:

(1) $T' - T$, *i. e.*, the elevation of temperature of the middle section of the sheet above the temperature of its two surfaces.

(2) Q, *i. e.*, the quantity of heat of vulcanization evolved up to the particular time, in calories per cc. After a certain period of time, $T' - T$ approaches zero, and Q becomes constant, and then defines the total thermal balance of vulcanization.

(3) The stiffness of the vulcanizate, expressed in grams per sq. mm. at an elongation of 300 per cent. It is sufficient to define in an approximate way the mechanical properties attained by the particular conditions of vulcanization.

Let us first consider a rubber mixture vulcanized without sulfur, but with 4 per

cent of tetramethylthiuram disulfide, and containing 10 per cent of zinc oxide (based on the rubber) as activator. The temperature of vulcanization was 143° C. The evolution of heat was at first very rapid (see Fig. 3), and if it had not been for an irregularity of heating because of the thickness, this would perhaps have been even more pronounced. A temperature elevation of 1.4° C. above that of the press was reached, a value which was quite exceptional for all the experiments. The evolution of heat then diminished rapidly, but by a different exponential law, as it was possible to verify from the experiments.

The changes in the mechanical properties ran strictly parallel to the quantities of heat evolved; after 70 minutes the evolution of heat was practically zero, while the plateau effect was very pronounced. The total heat evolved was 3.5 calories per cc., but this cannot be ascribed unreservedly to combination of rubber and sulfur, since the sulfur comes from the disulfide.

Vulcanization by tetramethylthiuram disulfide is perhaps the simplest type; the rate of vulcanization is a maximum at the beginning, and then diminishes gradually; furthermore the combined sulfur is relatively low.

Another rubber mixture containing a low concentration of sulfur was the following:

Rubber	100
Sulfur	0.8
Piperidinium pentamethylenedithiocarbamate	1
Zinc oxide	10

This mixture was vulcanized at 110° C. The heat evolved (see Fig. 4) was 0.6 calorie per cc., *i. e.*, approximately 0.8 calorie per cc. per 1 per cent sulfur. With cessation of evolution of heat, the mechanical stiffness of the vulcanizate became constant.

The mixture:

Rubber	100
Sulfur	2
Tetramethylthiuram monosulfide	0.22
Zinc oxide	10

was vulcanized at 110° C. Its heat of vulcanization diagram was extremely interesting and significant (see Fig. 5). Judged by plasticity measurements and by changes in mechanical properties, there is an initial period when vulcanization is retarded. The heat evolved followed the same trend, *i. e.*, it commenced at practically the same time that the dynamometer revealed the beginning of an appreciable stiffness, passed through a maximum value, and finally diminished to a negligible value, while the stiffness curve reached a plateau region.

The quantity of heat evolved was 2.5 calories per cc., *i. e.*, at least 1.25 calories per cc. per 1 per cent of combined sulfur. This value is approximately 50 per cent greater than the corresponding quantity of heat evolved by the preceding rubber mixture accelerated with piperidinium pentamethylenedithiocarbamate. Without continuing with further examples, where the values of combined sulfur are not known with any degree of precision, it may be concluded that by increasing the percentage of sulfur to 5.5 per cent, heats of vulcanization above 10 are obtained, in other words, at least 2 calories per cc. per 1 per cent of sulfur. Accordingly the hypothesis of Blake seems to be confirmed in a clearly defined experimental way, although it is better to await more decisive experiments in which every possible interference by secondary reactions has been avoided.

Vulcanization appears therefore to be always an exothermic reaction, and an evolution of heat accompanies the improvement in the mechanical properties. Conversely when this evolution of heat ceases, the mixture enters a plateau stage with respect to changes in mechanical properties. However, this plateau stage

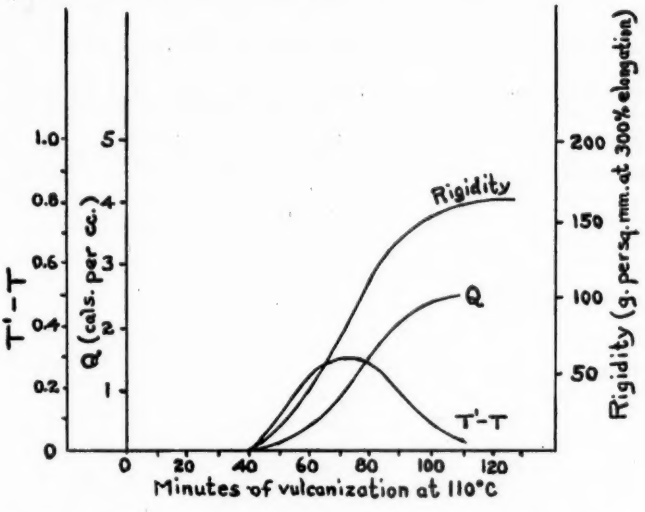

Figure 5—Mixture Containing 2 Per Cent Sulfur and Tetramethylthiuram Monosulfide

may be reached before the evolution of heat ceases (as indicated by later experiments which are to be repeated).

Conclusions

An experimental apparatus has been developed by means of which it is possible to measure with a high degree of precision the heats of vulcanization of rubber mixtures containing even very low percentages of sulfur, at temperatures as low as 110° C. Studies of vulcanization on a strictly thermochemical basis now appear both practicable and promising.

An evolution of heat of vulcanization is accompanied by an improvement in the mechanical properties of a rubber mixture. The quantity of heat evolved does not seem to be a linear function of the percentage of combined sulfur, at least for low percentages.

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Studies in the Vulcanization of Rubber

VII. Unsaturation of Rubber Vulcanized with Nitro Compounds and Benzoyl Peroxide[1]

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RUBBER is primarily an unsaturated hydrocarbon. Sulfur adds to its double bonds during vulcanization to form soft and hard vulcanizates. In the formation of soft vulcanized rubber, unsaturation is reduced several per cent by the chemical addition of sulfur. Spence and Scott (*10*) showed that the proportion of combined sulfur corresponds exactly to the decrease in unsaturation, and therefore that sulfur combination consists entirely of addition to the double bonds of rubber.

The studies of one of the authors (*1*) on the vulcanization of rubber with nitro compounds indicate that these substances or their decomposition products combine with rubber. Van Rossem (*8*) also showed that vulcanization with benzoyl peroxide is accompanied by a decrease in extractable material, indicating that either the reagent or its decomposition products combine chemically with the rubber. The natural expectation would be that addition to the double bonds occurs and that the unsaturation decreases correspondingly.

Van Rossem's proposed mechanism for the vulcanization with benzoyl peroxide would involve no change in unsaturation. Fisher and Gray (*2*) applied Kemp's method (*4*) in determining the iodine numbers of a single vulcanizate of each of four compounds. The vulcanizing agents involved were *m*-dinitrobenzene, trinitrotoluene, and benzoyl peroxide. Their unsaturation values agreed closely with calculated values for the unvulcanized compounds. They concluded from their results that "Ordinary vulcanization is an unknown or undetermined type of change in the hydrocarbon involving no change in the unsaturation and that chemical union of sulfur is a secondary reaction." If true, this evidence is a serious blow to the chemical theory of vulcanization which postulates that a chemical reaction is essential for the process. The present paper offers evidence that the vulcanization of rubber with these reagents does involve change in its unsaturation.

Experimental Procedure

There are a number of methods of determining the unsaturation of rubber. The early ones involved reacting it with an excess of bromine and titrating the excess reagent with potassium iodide and thiosulfate after a definite time period. Various authors have recommended differing conditions (*6*, *9*, *11*). The reaction is complicated, however, by the substitution of some of the hydrogen of the rubber by bromine. Lewis and McAdams (*7*) suggested that the hydrogen bromide formed by the substitution be titrated with potassium iodate and sodium thiosulfate. If this correction is applied to the total bromine absorption, values are obtained that are approximately correct, but conditions have to be controlled carefully if precise results are to be obtained. Kemp suggested the reaction of rubber with iodine chloride at 0°. Under these conditions satisfactory results are obtained, and this is probably the best method yet offered.

Nitro compounds react with rubber so weakly that only soft vulcanized rubber can be formed. Ebonite cannot be produced with this reagent. It was thought at first that, since iodine chloride is sufficiently active to react completely with rubber at 0° C., the reagent might displace any combined nitro compound to give the impression that no combination had occurred. This might explain the anomalous results of Fisher and Gray. The first part of this paper contains work with iodine bromide, a reagent less vigorous than iodine chloride, with the idea of overcoming the above difficulty. The second part contains work with iodine chloride. Substantially the same results were obtained in both cases.

Iodine Bromide

Iodine is too inactive a reagent to add completely and saturate all the double bonds in rubber. Iodine bromide is intermediate in activity between iodine and iodine chloride. Gorgas (*3*) claimed that iodine bromide makes a very satisfactory agent for determining unsaturation. The regular Hanus reagent consists of a solution of iodine bromide in glacial acetic acid. Gorgas found that this gave low values, perhaps because of the coagulating effect of the acid on the rubber solution. With carbon tetrachloride as the solvent, better results were obtained, but a rapid increase occurred in unsaturation values with reaction time. Kemp found that at 0° C. the rate of addition of this reagent was too slow to make its use feasible. At room temperatures following Gorgas' procedure, Kemp and Mueller (*5*) obtained low values, but by using a larger excess of reagent and a longer reaction time they obtained better results. The results were sufficiently variable, however, so that they believed the method could not be relied upon for a high degree of accuracy.

Gorgas used 0.2 *N* solutions but in the present work reagents of half this strength were used. The carbon tetrachloride was

purified by treating with alcoholic sodium hydroxide, washing with water, drying with C. P. calcium chloride, and distilling fractionally. Exactly 0.1 *N* solutions of iodine and bromine in this solvent were then prepared and standardized with aqueous sodium thiosulfate. Equal volumes were mixed to form the iodine bromide solution. This was standardized against sublimed arsenious oxide.

The determination of the unsaturation of unvulcanized rubber was carried out by refluxing the sample for 2 hours in C. P. carbon tetrachloride. Vulcanized samples were not dissolved sufficiently by this treatment. *p*-Dichlorobenzene was used as the solvent since it disintegrates most vulcanized samples at its boiling point (172° C.) and does not react with the reagent. Since it is a solid at room temperature, carbon tetrachloride must be added after cooling to maintain a liquid solution.

A study of the suitability of the method involved an investigation with a substance of known behavior. Samples of smoked sheet of known weight were swelled in the solvent in covered Erlenmeyer flasks. A measured amount of the iodine bromide solution was added, and the mixture was allowed to stand in darkness for a definite period at room temperature (22° to 25° C.), 50 cc. of 10 per cent aqueous potassium iodide were added, and the excess halogen was titrated with aqueous sodium thiosulfate. As the end point approached, starch solution was added and small amounts of acetic acid were used to destroy the emulsion. With practice, reproducible results can be easily obtained.

A series of determinations was made on 0.1-gram samples from a single batch of smoked sheet with varying times of reaction and with different excesses of reagent. Each sample was extracted with acetone after weighing, and the acetone was removed in a vacuum desiccator before solution in the solvent. It is generally accepted that rubber hydrocarbon is composed of C_5H_8 units, each containing one double bond. The theoretical iodine number of this hydrocarbon is then 372.8. Since the hydrocarbon content of rubber is 93 to 96 per cent, the iodine number of raw rubber should be 347 to 358:

Reaction Time	Excess IBr	Iodine No.	Reaction Time	Excess IBr	Iodine No.
Min.	%		*Min.*	%	
15	39	265	60	110	348
	64	290		135	345
				138	351
30	65	310		188	354
	308	359		210	356
				356	366
60	56	312			
	92	340	120	250	378
			180	241	388

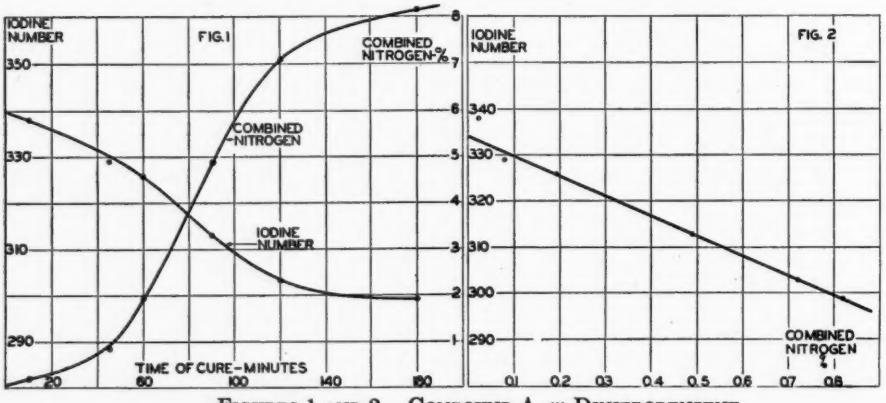
From these results it may be concluded that, if less than 100 per cent excess reagent is used and if the reaction time is less than 60 minutes, the action is incomplete. Increasing the excess beyond 200 per cent and the time beyond 60 minutes gives values which are too high.

Compound A (smoked sheets 100, litharge 5, and *m*-dinitrobenzene 10) was vulcanized for varying periods of time at 132° C. (270° F.). Unsaturation values were determined as above, using 200 per cent excess reagent, a 60-minute reaction time, and *p*-dichlorobenzene as the solvent. Experiments showed that neither *m*-dinitrobenzene nor litharge is affected by iodine bromide.

In order to compare the change in unsaturation with the chemical effect of the reaction with dinitrobenzene, combined nitrogen values were determined on other samples of the same cures after similar acetone extraction. The nitrogen values were corrected for the blank on the raw unvulcanized rubber after acetone extraction and calculated on the base of rubber in the compound:

270° F. Vulcanization *Min.*	Iodine No.	Combined N %
10	338	0.027
45	329	0.082
60	326	0.197
90	313	0.483
120	306	0.720
180	299	0.822

There seems to be a progressive decrease in unsaturation during vulcanization as determined by this method, and this is accompanied by an increase in combined nitrogen. In Figure 1 both sets of values are plotted against the time of vulcanization. If the theory is correct that the two effects



FIGURES 1 AND 2. COMPOUND A, *m*-DINITROBENZENE

are proportional, plotting the iodine number against combined nitrogen should give a straight line. These data are delineated in Figure 2 and produce a straight line within the limits of the experimental error.

Iodine Chloride

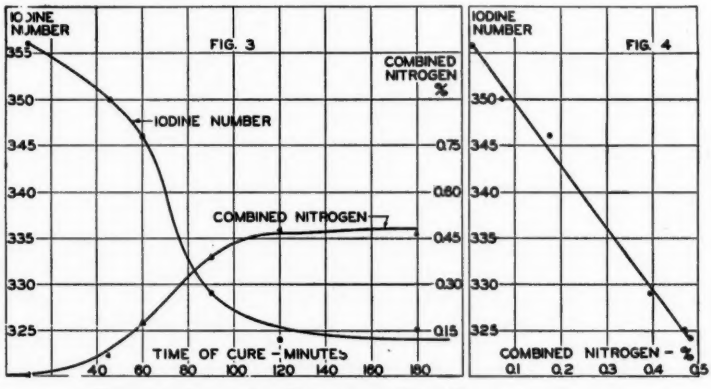
Iodine chloride was used in following the unsaturation for several compounds. The composition of these compounds is as follows:

	B	C	D	E	F
Smoked sheet	100	100	100	100	100
Litharge	5	5	...	...	...
m-Dinitrobenzene	6	...	...	...	...
sym-Trinitrobenzene	...	6	...	...	...
Benzoyl peroxide	...	...	7	11.1	25

These vulcanizates had tensile strengths of 1000 to 2000 pounds per square inch.

In Kemp's procedure for determining the unsaturation with iodine chloride, tetrachloroethane was used as the solvent for disintegration of the samples. A number of blanks were run on this material, heating them exactly as Kemp prescribed. No matter how carefully the tetrachloroethane was purified, enough decomposition was found at its boiling point to introduce serious errors. Tests on C. P. *p*-dichlorobenzene indicated that this material is completely stable at its boiling point. Tests lasting up to 5 hours indicated that the time of boiling of this reagent with rubber has no effect on the unsaturation determination. Therefore, this reagent was substituted for the tetrachloroethane in the present determinations.

One-tenth-gram samples of the vulcanizates were acetone-extracted and added to 50 grams of *p*-dichlorobenzene, and



FIGURES 3 AND 4. COMPOUND B, *m*-DINITROBENZENE

the mixture was boiled until disintegration was complete. After cooling, 50 cc. of C. P. carbon disulfide were added to assure a liquid solution. The mixture in watch-glass-covered flasks was chilled in ice for 30 minutes. One hundred per cent excess of 0.2 *N* iodine chloride in glacial acetic acid was added with stirring. After a 2-hour reaction period at 0° C., 25 cc. of 15 per cent aqueous potassium iodide and 50 cc. of water were added. The excess halogen was determined with 0.1 *N* aqueous sodium thiosulfate. Emulsions were broken with small amounts of ethyl alcohol. Tests indicated that ethyl alcohol had no effect on the determination. Blanks were run on the reagents in the usual manner. The iodine numbers on duplicate samples normally checked to within less than four units. It was found that the acetone remaining in the rubber sample after extraction was completely volatilized in the disintegration so that the acetone did not need to be removed previously. It was also determined that during the reaction period with iodine chloride no vapors of halogen were lost from the covered flasks.

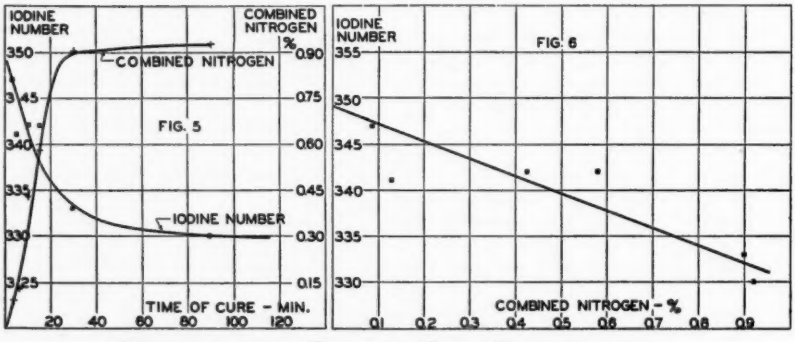
The nitrogen content of the various cures of compounds B and C was determined by a micro-Kjeldahl method on acetone-extracted samples. The amount of acetone-soluble material

was determined on compounds D, E, and F, and from these values the amount of products from the benzoyl peroxide which combined with the rubber was calculated. In the following table these values are listed as combined benzoyl peroxide. All analytical data are calculated on the basis of the raw rubber in the compound.

Compound B			Compound C		
270° F. Vulcanization	Combined N	Iodine No.	245° F. Vulcanization	Combined N	Iodine No.
Min.	%		*Min.*	%	
10	0.000	356	3	0.089	347
45	0.070	350	5	0.129	341
60	0.174	346	10	0.427	342
90	0.395	329	15	0.581	342
120	0.480	324	30	0.900	333
180	0.466	325	90	0.921	330

Benzoyl Peroxide Compounds Vulcanized 20 Min. at 275° F.

Compound	Benzoyl Peroxide		Iodine No.
	Total	Combined	
D	7.0	2.31	341
E	11.1	5.31	333
F	25.0	13.97	311



FIGURES 5 AND 6. COMPOUND C, *sym*-TRINITROBENZENE

These data are plotted in Figures 3 to 7. The procedure used in the present work is somewhat different from that of Fisher and Gray. They swelled the vulcanizates in carbon disulfide for 24 hours at room temperature and then allowed the iodine chloride to react for 24 hours at 0° C. in the dark, or twelve times as long as the above experiment.

The effect of this long reaction period was examined by allowing iodine chloride to act on vulcanizates of compound B for 24 hours at 0° C. The iodine numbers showed that the long time of treatment changes the absolute values somewhat, but the slope of the line relating combined nitrogen and unsaturation was almost exactly the same as that in Figure 4. An unusually long time of acetone extraction had no effect on the iodine number or the per cent combined nitrogen.

The possibility that the decrease in unsaturation might be attributed to a reaction of the double bonds of the rubber with one another or, in the case of compounds B and C, a

reaction of the double bonds with litharge was investigated. The following table contains the results of these experiments:

Compound		270° F.	Iodine No.
Rubber	PbO	Heat Treatment	(Not Acetone-Extd.)
%	%	*Min.*	
100	0	None	352
100	0	120	350
95	5	None	350
95	5	120	351

An increase in unextractable nitrogen during the vulcanization with nitro compounds might be explained as being due to a reaction of the nitro compound and the nonrubber constituents, or a reaction between the nitro compound and the litharge to form a material insoluble in acetone. These possibilities cannot be rejected definitely. It was shown, however, that on heating a mixture of litharge and *m*-dinitrobenzene no acetone-insoluble nitrogenous material was formed.

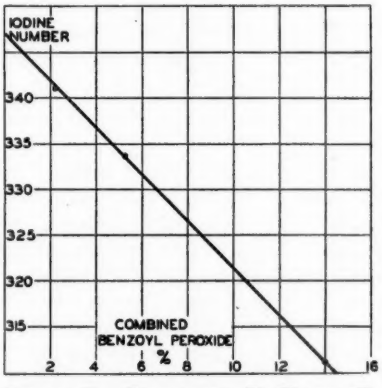


FIGURE 7. COMPOUNDS D, E, AND F, BENZOYL PEROXIDE

Discussion

The data show an approximately linear relation between the per cent combined vulcanizing agent and the unsaturation of the rubber in the compound. These results obtained through the use of two independent analytical methods are at variance with those of Fisher and Gray. The present experiments seem to indicate that during the vulcanization of rubber with polynitro compounds or benzoyl peroxide, the reagents or products from them add chemically to the double bonds of the rubber hydrocarbon. There is no evidence in these experiments nor is there any in the case of sulfur vulcanization to indicate whether the vulcanizing agents add to the double bonds in a single molecule or bridge between double bonds in adjacent molecules, thereby increasing molecular size.

It is possible that, contrary to the experiments with sulfur, a single molecule of the present vulcanizing agents adds to more than one double bond. The double bonds saturated per molecule of vulcanizing agent may be calculated by the following formula:

$$\frac{100\,(I_0 - I_t)M}{68\,(I_0)W} = \text{double bonds saturated per molecule of nitro compound or benzoyl peroxide, or atom of sulfur or selenium}$$

where I_0 and I_t = iodine numbers at vulcanization times of 0 and t, respectively

M = molecular weight of nitro compound or benzoyl peroxide, or atomic weight of sulfur or selenium

W = weight of vulcanizing agent combined with 100 grams of rubber

The number of double bonds saturated per molecule of vulcanizing agent was calculated as follows:

Vulcanizing Agent	Unsaturation Reagent	Double Bonds Satd. per Mol. of Reagent
m-Dinitrobenzene	IBr	5.4
m-Dinitrobenzene	ICl	7.5
sym-Trinitrobenzene	ICl	3.2
Benzoyl peroxide	ICl	2.6

Preliminary data indicate that an atom of selenium saturates about 6 double bonds.

A molecule of *m*-dinitrobenzene appears to saturate a fairly large number of double bonds. It was perhaps to be expected that a molecule of trinitrobenzene would saturate more double bonds than the dinitro compound, but this does not seem to be true. A molecule of benzoyl peroxide also saturates more than one double bond. It is possible that these results may be explained by the theory that vulcanizing agents produce some sort of cyclization. The quantitative implications of the data need more study.

The qualitative implications of these data are important, indicating that we have yet to find a vulcanization in which a chemical reaction does not take place, and thereby give more support to the chemical theory of vulcanization.

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High-Speed Vulcanization of Rubber

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PRIOR to about 1906 when organic accelerators were first employed in the tire industry, vulcanization practice for soft rubber generally involved the use of larger amounts of sulfur than is now customary. Acceleration of vulcanization was obtained by the use of liberal amounts of one or more of the oxides of zinc, calcium, magnesium, or lead. As the new and faster organic accelerators have been employed, the amount of sulfur used has been gradually decreased until it now ranges from about 0.5 to 5 per cent of the rubber; the general tendency is towards the use of the smaller quantity.

In the rubber-insulated-wire industry in this country, it is becoming general practice to employ the Western Electric Company's continuous vulcanizing process (*1*) whereby highly accelerated soft-rubber insulating compositions are completely vulcanized at 198° C. in a few seconds on the wire as it passes continuously at high speed from the insulating machine through a long pipe filled with steam under about 200 pounds per square inch (14.1 kg. per sq. cm.) pressure. This process is rapidly displacing the older one of coiling the insulated wires on drums or in pans filled with soapstone powder and vulcanizing in large autoclaves for periods of 1 to 5 hours under 20 to 40 pounds steam pressure (126° to 142° C.). The continuous process eliminates the objectionable soapstone dust and produces more uniformly vulcanized wire which is free from crossover defects and flattening of the insulation. The process also provides attractive economies in manufacture.

The literature reveals practically no information on the rate of vulcanization and quality of soft rubber vulcanized at temperatures ranging from 170° to 200° C. Many investigators, however, have studied the effect of temperature on rate of vulcanization and quality of the vulcanizate at temperatures below 170° C. Recently, for example, Shepard and Street (*13*) reviewed this subject and found that the optimum tensile properties of tire tread compounds did not vary when vulcanized at temperatures ranging from 127° to 160° C. They found that the aging quality tended to decrease as the temperature of vulcanization increased.

The purpose of the present paper is to present comparative data on the rate of vulcanization of soft rubber and on the

quality of the product vulcanized in direct steam at temperatures ranging from 142° to 198° C.

Because of the difficulties involved in vulcanizing suitable test sheets of rubber in open steam, it was decided to prepare lengths of wire and use tubular insulation specimens for test purposes. These test specimens have the advantage of being directly comparable with insulated wire produced by the continuous vulcanizing process. The basic rubber compound selected for this investigation has suitable plastic properties for extrusion as a smooth covering on the conductor. When vulcanized, it has high tensile strength and cutting resistance. Using the base compound selected, three amounts of sulfur were added—namely, 1.0, 2.5, and 4.0 per cent of the rubber with suitable adjustments in accelerator and retarder content

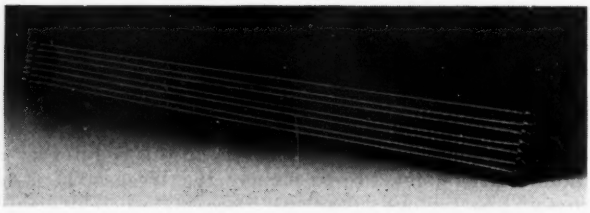

FIGURE 1. RACK WITH WIRES MOUNTED FOR USE IN THE VULCANIZER

in order to obtain approximately equal curing rates. Cures were made for varying lengths of time at 142°, 170°, 185°, and 198° C. in open steam. The compounds used were as follows:

Ingredients	Compound 1	Compound 2	Compound 3
Pale crepe	100.00	100.00	100.00
Lithopone (standard 30% ZnS)	125.00	125.00	125.00
Zinc oxide (fast-curing type)	25.00	25.00	25.00
Stearic acid	1.00	1.00	1.00
Phenyl-α-naphthylamine	2.00	2.00	2.00
Sulfur	4.00	2.50	1.00
Litharge (sublimed)	1.00	1.00	1.00
Tetramethylthiuram monosulfide	0.50	0.75	2.00
Di-o-tolylguanidine	....	0.25	0.50
	258.50	257.50	257.50

The compounds were mixed in batches of about 1550 grams each in a size B Banbury mixer. The rubber was placed in the mixer and broken down for 1 minute. The zinc oxide, antioxidant, sulfur, and stearic acid were then added, and mixing was continued for 3 minutes. The lithopone was added, and mixing was continued for 7 minutes. The batch was then placed on a cool laboratory mill; after 2-minute mastication the accelerator and litharge were added, and the compound was finally refined four times through tight rolls, followed by 6 more minutes of milling.

Preparation of Samples

A seventeen-gage tinned bronze conductor was insulated to an outside diameter of approximately 0.28 cm. at an extrusion speed of about 14 meters per minute, using a No. $^1/_2$ Royle machine. Lengths of insulated wire about 1 meter long were mounted on racks as shown in Figure 1 for vulcanizing. Vulcanization was carried out in the apparatus shown in Figures 2 and 3.

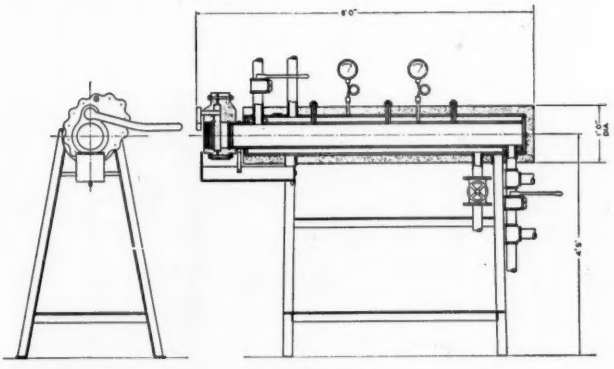

FIGURE 2. DIAGRAM OF VULCANIZING TUBE

The vulcanizing chamber consists essentially of a 1.5-meter length of 5-inch extra heavy wrought-iron pipe located centrally within a somewhat shorter length of 8-inch extra heavy pipe which serves as a steam jacket. To one end of both pipes is welded a steel plate. The jacket pipe is welded to the inner pipe 6.25 cm. from the other end. Access to the inner pipe or vulcanizing chamber is obtained by means of a standard 5-inch Everlasting Model W straight-lever type of valve having an iron body with screw ends for a working steam pressure of 250 pounds per square inch (17.6 kg. per sq. cm.). Steam enters and is released from the vulcanizer by 1.5-inch Powell Giant lever throttle valves for 350 pounds (24.6 kg.) working steam pressure. Suitable pressure gages, auxiliary valves, and traps are shown in Figure 2. Steam at pressures up to 250 pounds per square inch pressure is supplied by a type S. A. Kane fire tube boiler operating at 7 horsepower. The vulcanizing tube is mounted on suitable iron supports and is well insulated with asbestos.

Before using the apparatus for vulcanizing, steam at a pressure equivalent to the desired temperature is allowed to enter the jacket and vulcanizing tube. After 30 minutes or a time sufficient to ensure that the apparatus is heated to the desired temperature, the steam is discharged from the inner vulcanizing tube. It is customary for two men to operate the apparatus. The end valve is opened, a rack on which wire samples are mounted is placed in the tube, and the valve is closed. The second operator opens the quick-action steam valve and simultaneously sets a stop watch. The desired steam pressure is reached in the tube in a fraction of a second. When the time for vulcanization has elapsed, he closes the steam valve. The other operator opens the quick-action exhaust valve and then the end valve to the vulcanizing tube, and removes the rack by means of a hooked rod. It is estimated that the time involved in attaining temperature in the tube is less than 1 second, and for exhausting and opening the tube about 1 second.

Conductors were insulated with the three compounds and vul-

canized in the manner described. Cures were made over the temperature ranges indicated and in the range near maximum tensile properties, for the most part at the following time intervals:

Steam Pressure		Equivalent Temp.	Time Range	Time Interval
Lb./sq. in.	*Kg./sq. cm.*	° *C.*		
40	2.8	142	6–35 min.	2 min.
100	7.0	170	50–140 sec.	5 sec.
150	10.5	185	15–50 sec.	3 sec.
200	14.1	198	8–40 sec.	2 sec.

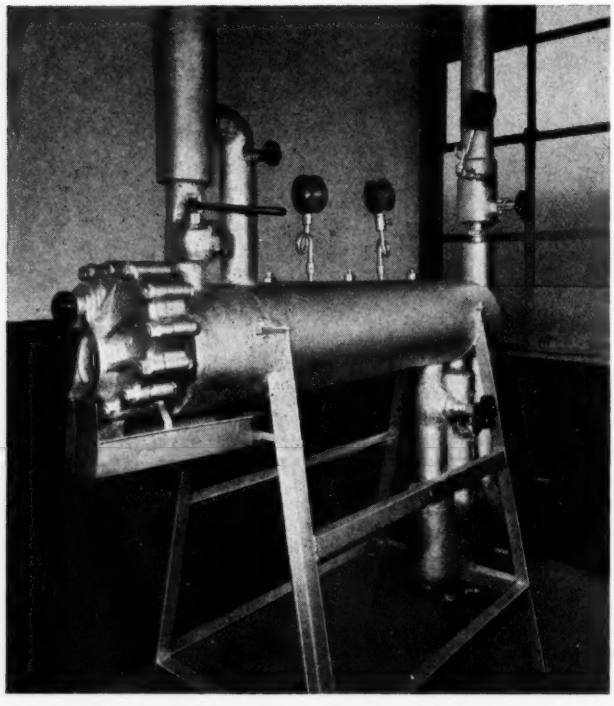

FIGURE 3. HIGH-PRESSURE VULCANIZING TUBE

After vulcanizing, the wires were allowed to rest at room conditions of temperature and humidity for at least 18 hours before specimens were selected for test. Five tensile-test specimens 15 cm. long were taken, representing original tests at each cure for each compound. Similarly, specimens representing cure to approximately maximum physical properties were selected for test after 48 and 96 hours of accelerated aging at 80° C. and 3.5 kg. per sq. cm. oxygen pressure. Three groups of four specimens each were selected for these original and aged compression tests. Compression tests were made in addition to tensile tests because the compression resistance or crushing load of rubber insulation on wire is frequently more important than tensile properties. In order to facilitate removal of the insulation from the tinned conductors for tensile test, the specimens were immersed in mercury to amalgamate the tin coating previous to

test. The insulation was not removed from the conductors until after accelerated aging. The tubular lengths of insulation were used as tensile test specimens.

Tensile strength, modulus, and per cent elongation at break were determined on a Scott tensile tester. The values reported are, for the most part, averages of the five values obtained. Compression tests were made on the Bell Telephone Laboratories machine manufactured by the Henry L. Scott Company (*5*). Values reported are the average of four tests.

Effect of Curing Temperature on Tensile Properties and Compression Resistance

Physical data on the three compounds as affected by increasing vulcanizing temperature and time are given in Table I and Figures 4 and 5. It is evident from these data that the tensile properties of the compounds vulcanized at 185° and 198° C. are practically equivalent to those of the same compounds vulcanized at 142° and 170° C. At all vulcanizing temperatures except 170° C., the tensile properties of compounds 2 and 3 are superior to those of compound 1. At 170° C. the tensile properties of all three compounds at their best cures are substantially the same. Compounds 2 and 3 are superior to 1 in the flatness of their curing curves at all vulcanizing temperatures, although the differences at 170° C. are not very marked.

The compression resistance data are interesting because they show that the maximum values for compounds 1 and 2 are higher than for 3 when vulcanized at temperatures above 142° C. At 142° C., however, compound 1 gives the lowest compression resistance. In general, the results indicate some advantage for the higher vulcanizing temperature when better compression resistance is desired.

Effect of Curing Temperature on Accelerated Aging

Because of the increased effectiveness found for accelerated aging in oxygen at 80° C. (*6*), this temperature was used for this series instead of 70° C. Oxygen pressure of 3.5 kg. per sq. cm. was used because higher pressures do not appreciably increase the aging rate (*6*). The changes in tensile strength and in compression resistance which resulted from accelerated aging for each of the four curing temperatures investigated are shown in Table II and Figure 6. Evaluation by means of compression resistance indicated less deterioration on aging than did evaluation by tensile tests.

The compound containing 4.0 per cent sulfur showed better aging properties when cured at 185° and 198° C. than at 142° and 170° C. The other two compounds aged about the same, regardless of vulcanization temperature.

Temperature Coefficient of Vulcanization Velocity

For some time it has been recognized that the temperature of cure for soft rubber is proportional to the log of the time

TABLE I. EFFECT OF TIME OF CURE ON TENSILE STRENGTH, ELONGATION, MODULUS, AND COMPRESSION RESISTANCE

Compound 1						Compound 2						Compound 3					
Time of cure	Tensile strength	Elongation at break	Modulus at elongation Of 300%	Modulus at elongation Of 500%	Compression resistance	Time of cure	Tensile strength	Elongation at break	Modulus at elongation Of 300%	Modulus at elongation Of 500%	Compression resistance	Time of cure	Tensile strength	Elongation at break	Modulus at elongation Of 300%	Modulus at elongation Of 500%	Compression resistance
Sec.	*Kg./sq. cm.*	*%*	*Kg. per sq. cm.*		*Kg.*	*Sec.*	*Kg./sq. cm.*	*%*	*Kg. per sq. cm.*		*Kg.*	*Sec.*	*Kg./sq. cm.*	*%*	*Kg. per sq. cm.*		*Kg.*
									Cured at 142° C.								
15[a]	198.6	560	50.7	149.6	627	6[a]	83.6	550	6.8	37.3	431.0	9[a]	269	570	74.0	136.0	368
20[a]	258.5	600	66.5	183.1	705	8[a]	103.5	640	13.8	55.7	400.0	12[a]	265	580	66.2	203.0	619
25[a]	249.3	560	79.2	200.0	745	10[a]	130.0	590	24.0	85.0	435.0	14[a]	294	600	68.0	202.7	660
30[a]	202.8	500	77.7	192.9	709	12[a]	168.5	610	30.6	109.0	473.0	16[a]	280	600	65.0	203.0	641
35[a]	202.1	520	76.4	196.4	695	14[a]	204.0	600	38.8	132.0	542.0	18[a]	287	600	64.0	196.0	621
						16[a]	239.0	590	54.3	168.0	578.0	22[a]	290	620	68.5	186.0	628
						20[a]	280.0	540	86.7	237.0	661.0	28[a]	282	600	61.2	195.0	646
												35[a]	267	600	59.5	183.5	608
									Cured at 170° C.								
60	198.9	630	37.7	122.9	564	60	234.0	600	48.6	160.0	565.0	50	61	460	26.6	...	377
80	296.5	590	77.8	211.2	636	70	284.0	560	78.2	228.0	790.0	60	112	430	..	162.3	417
100	282.4	600	70.4	200.0	750	75	290.0	570	76.6	224.0	809.0	65	111	450	41.2	...	422
120	168.3	480	72.1	...	700	80	283.0	550	85.0	236.0	720.0	70	263	540	78.1	217.0	468
140	172.2	460	72.5	...	723	90	298.0	570	80.0	231.0	687.0	75	270	540	80.5	228.0	600
						100	292.0	570	84.0	230.0	731.0	80	273	560	75.0	214.0	650
						120	281.0	540	92.0	238.0	710.0	90	296	600	69.4	207.0	676
												100	286	590	67.8	205.0	664
									Cured at 185° C.								
20	223.6	610	42.2	141.5	600	15	136.0	630	22.5	80.4	437.0	15	56	520	13.5	...	268
25	252.8	600	52.1	171.8	623	18	160.5	630	32.8	95.5	468.0	20	56	520	12.9	45.8	322
30	246.2	570	62.0	192.9	695	21	203.0	620	37.0	124.0	571.0	24	111	550	25.7	82.2	391
33	233.4	550	64.8	193.2	695	24	252.0	600	53.8	173.5	635.0	27	244	570	62.0	190.2	387
36	239.4	550	66.9	200.7	699	27	281.0	600	62.0	208.0	667.0	30	252	570	71.1	204.0	426
39	225.3	530	67.7	200.7	741	30	302.0	570	76.7	236.0	679.0	33	249	560	72.0	202.5	597
45	209.5	520	66.4	202.4	755	35	391.0	550	77.4	236.0	758.0	36	259	560	72.0	207.0	568
50	217.6	540	63.0	182.4	709							40	262	560	67.5	202.5	609
									Cured at 198° C.								
8	102.1	560	44.1	...	368	8	124.3	600	20.8	80.0	428.0	8	51	600	10.6	37.0	295
10	190.0	600	40.0	126.7	505	10	132.0	610	24.1	83.0	440.0	10	84	590	15.8	58.0	299
12	214.4	580	46.8	150.3	536	12	199.0	610	38.7	130.0	503.0	12	111	560	24.7	84.0	395
14	258.1	610	52.8	166.2	604	14	262.0	590	57.8	187.0	573.0	14	203	490	72.0	194.0	427
16	264.4	600	58.4	174.3	627	16	284.0	580	70.5	212.0	682.0	16	271	560	72.3	208.0	532
18	215.1	540	65.1	186.2	645	18	291.0	560	80.0	236.0	668.0	20	275	560	72.3	213.0	663
20	219.0	500	81.3	208.4	795	20	293.0	550	85.5	239.0	723.0	25	278	580	66.0	201.5	618
30	192.9	510	72.5	186.6	795	25	285.0	550	80.0	231.0	723.0	30	279	580	64.0	201.5	628
40	169.0	510	63.3	...	700												

[a] Minutes.

TABLE II. EFFECT OF CURING TEMPERATURE ON ACCELERATED AGING

Time of Cure	Temp. of Cure	Tensile Strength — Original		Tensile Strength — At 80° C. and 3.5 Kg./Sq. Cm. O_2 — 48 hr.		Tensile Strength — At 80° C. and 3.5 Kg./Sq. Cm. O_2 — 96 hr.		Change in Tensile Strength on Aging — 48 hr.	Change in Tensile Strength on Aging — 96 hr.	Compression Resistance — Original		Compression Resistance — At 80° C. and 3.5 Kg./Sq. Cm. O_2 — 48 hr.		Compression Resistance — At 80° C. and 3.5 Kg./Sq. Cm. O_2 — 96 hr.		Change in Compression on Aging — 48 hr.	Change in Compression on Aging — 96 hr.
	° C.	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.	Lb./sq. in.	Kg./sq. cm.	%	%	Lb.	Kg.	Lb.	Kg.	Lb.	Kg.	%	%
Compound 1																	
20 min.	142	3715	262	3140	221	2735	192	−15.4	−26.3	1550	705	1450	660	1300	590	− 6.4	−16.0
80 sec.	170	4215	298	3350	235	2680	188	−20.5	−36.4	1400	640	1300	590	1090	495	− 7.1	−22.1
30 sec.	185	3500	246	3690	259	2950	208	+ 5.4	−16.0	1530	695	1350	614	1240	564	−11.7	−18.9
16 sec.	198	3750	264	3385	237	2670	187	− 9.7	−28.8	1380	630	1410	610	1220	552	+ 2.1	−11.6
Compound 2																	
20 min	142	3985	280	3335	235	2915	206	−16.3	−26.8	1460	663	1650	750	1420	645	+13.0	− 2.7
90 sec.	170	4255	300	3230	228	2840	200	−24.0	−33.2	1510	687	1550	682	1360	618	− 0.6	−15.0
30 sec.	185	4285	302	3510	247	3040	213	−18.0	−29.0	1490	676	1520	690	1300	591	+ 2.0	−12.7
	198	4170	294	3245	229	2985	210	−22.1	−28.4	1590	722	1610	731	1410	641	+ 1.2	−11.3
Compound 3																	
14 min.	142	4175	294	3645	250	3260	230	−15.0	−21.9	1450	660	1450	660	1460	663	0.0	+ 0.7
80 sec.	170	3890	273	3310	234	3155	222	−14.9	−18.8	1430	650	1510	687	1480	672	+ 5.6	+ 3.5
40 sec.	185	3720	262	3265	230	3285	231	−12.2	−11.6	1340	607	1450	660	1400	637	+ 8.2	+ 4.4
20 sec.	198	3900	274	3360	237	3250	229	−13.8	−16.6	1460	663	1370	623	1410	639	− 6.1	− 3.4

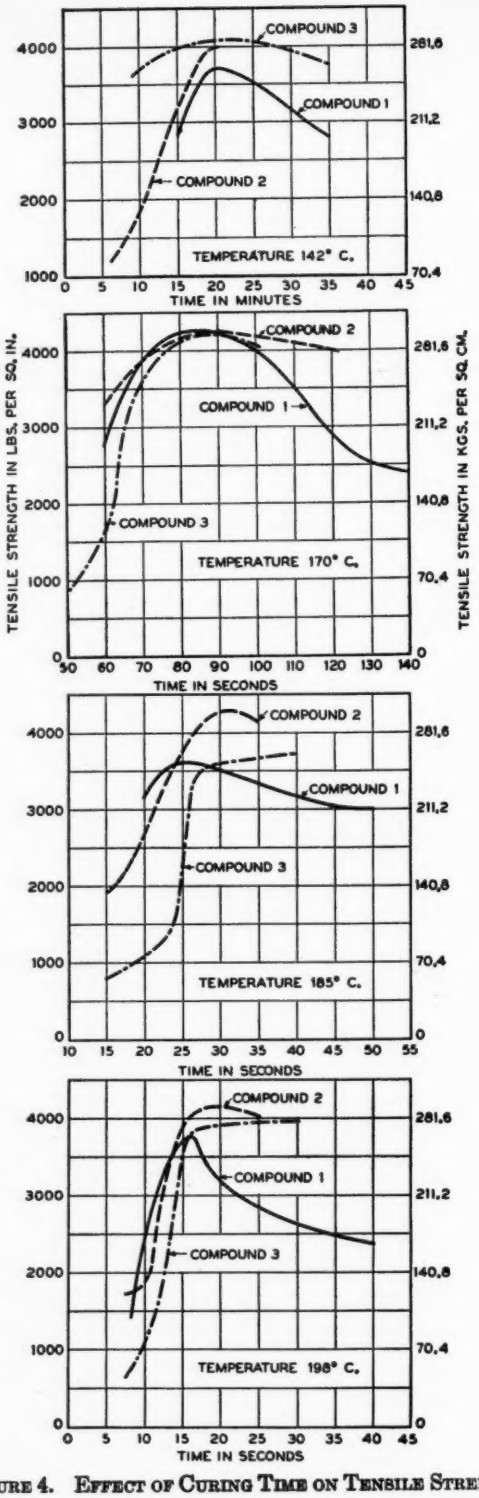

FIGURE 4. EFFECT OF CURING TIME ON TENSILE STRENGTH

of equivalent cures at various temperatures. However, there has been considerable disagreement as to the precise relationship existing, probably because of variations in experimental conditions employed and in some cases to less precise measurements as indicated by Sheppard (*14*).

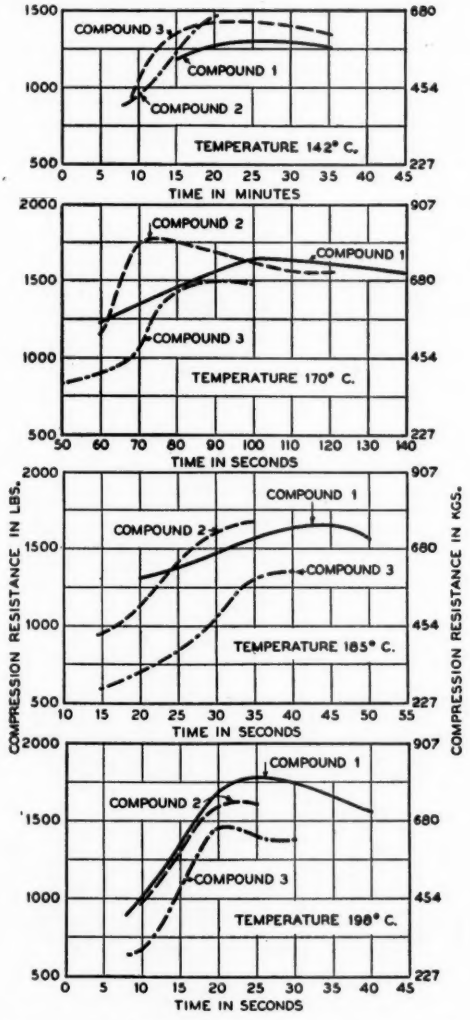

FIGURE 5. EFFECT OF CURING TIME ON COMPRESSION RESISTANCE

Investigations of the time-temperature relationship in the vulcanization of soft rubber have been confined to temperature ranges below 171° C. Investigations have also been previously confined to rubber compounds containing 2.5 or higher percentages of sulfur based on the rubber

In studies of this nature other investigators have not considered the time required for heating rubber to the vulcanization temperature. Since other studies have usually been confined to temperatures of 160° C. or lower, this time period

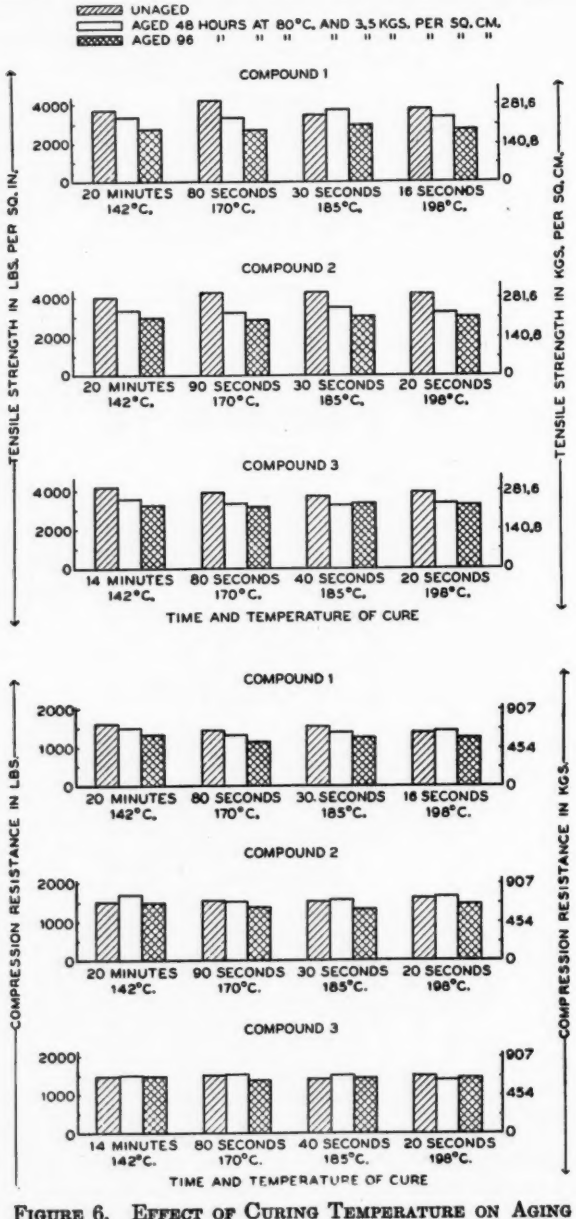

FIGURE 6. EFFECT OF CURING TEMPERATURE ON AGING (TENSILE STRENGTH AND COMPRESSION RESISTANCE)

in the case of thin sheets is small in comparison with the overall time of vulcanization. Since the present investigation, however, involves much higher vulcanization temperatures, it is necessary to make a time correction for heating because the time required to heat up to a temperature gradient of rapid cure is a considerable part of the total period required for cure.

In order to determine the time lag preceding active vulcanization of the insulated conductors, lengths of the wire were

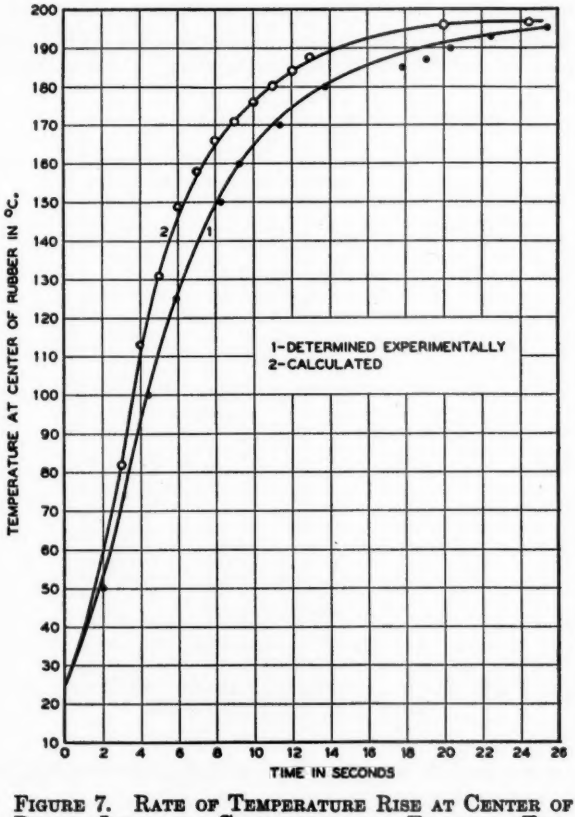

FIGURE 7. RATE OF TEMPERATURE RISE AT CENTER OF RUBBER-INSULATED CONDUCTOR WITH EXTERNAL TEMPERATURE OF 198° C.

heated in the vulcanizer at 198° C. for periods from 2 to 12 seconds, increasing by 1-second increments. Finger tests and compression tests on these wires indicated that active cure commenced after a little more than 7 seconds of heating.

The rate of heat transfer through the insulation was determined experimentally on lengths of insulation into which a thermocouple had been inserted after removal of the conductor. The thermocouple fitted tightly in the space previously

occupied by the conductor. Temperature readings were made with the aid of a potentiometer. For convenience a molten salt bath at 198° C. was used for heating. The time which elapsed from the moment of immersion until attainment of various temperatures was measured with a stop watch. The values as determined are plotted in the lower curve of Figure 7.

The upper curve in Figure 7 represents calculated temperatures at the center of the wire. These calculations were made according to the method of Williams (*18*) and to the data of Williamson and Adams (*19*) for a long cylinder. The assumption was made that the insulated conductor was a solid cylinder of the rubber insulating compound. The following for-

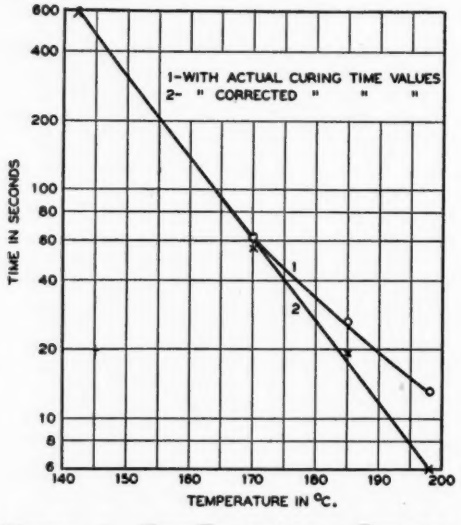

FIGURE 8. TIME-TEMPERATURE RELATION FOR MODULUS OF 2500 POUNDS PER SQUARE INCH (175 KG. PER SQ. CM.) AT 500 PER CENT ELONGATION FOR COMPOUND 3

mula was used for the calculations, substituting various values for t and solving for T:

$$\frac{T - T_1}{T_0 - T_1} = f\left(\frac{Dt}{r^2}\right)$$

where T = temperature at center of rubber cylinder in t seconds
T_1 = temperature of steam in vulcanizer, 198° C.
T_0 = original uniform temperature of rubber, 25° C.
D = diffusivity of rubber compound, 0.00095
t = time, seconds
r = half of insulated-wire diameter, 0.14 cm.

The correlation between experimental and calculated data, as shown in Figure 7, is considered to be good.

The time lag of about 7 seconds, as determined by compression tests on the wire heated at 198° C., corresponds on the experimental heating curve to a temperature of about 140° C. for the rubber in the center whereas the total time required for optimum cures is only 20 seconds. It appears reasonable to assume that the rate of vulcanization when this temperature gradient is set up in the rubber is not appreciable as compared with the rate after a few more seconds of heating.

Calculations indicate that the internal temperature of the rubber will follow similar time-temperature curves when heated at the other temperatures used for vulcanization. These calculations also indicate that comparable temperature gradients will be set up in the rubber at the various curing temperatures used in approximately the same 7-second

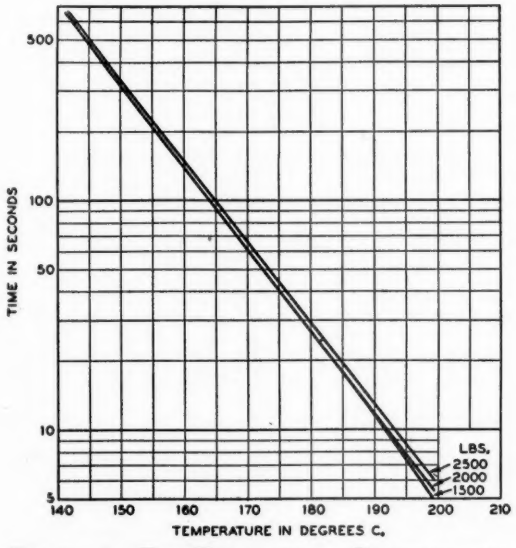

FIGURE 9. TIME-TEMPERATURE RELATION FOR CONSTANT VALUES OF MODULUS AT 500 PER CENT ELONGATION (COMPOUND 3)

period. Therefore, in calculating vulcanization rates, a correction of 7 seconds was made in the time of cure indicated for attaining each of the criteria used for each curing temperature. Data plotted in Figure 8 illustrate the justification for this procedure. The curved line represents uncorrected time values and the straight line, corrected time values.

Physical characteristics were taken rather than free sulfur content as criteria of cure for measuring curing rates. Shepard and Krall (*12*) and Eliel (*4*) indicated the advantages of physical tests for this purpose. The method of Sheppard (*14*) was used to determine the time required to double or halve the state of cure. The time required at various curing

TABLE III. TIME-TEMPERATURE RELATIONS FOR COMPOUNDS 1 AND 2

	Value of Property, Kg./Sq. Cm.	Seconds to Attain Properties	° C. to Halve or Double Time of Cure	No. of Reliable Points on Curve	Product of Two Preceding Figures	Av. No. of ° C. to Halve or Double Cure	Temp. Coefficient	Value of Property, Kg./Sq. Cm.	Seconds to Attain Properties			° C. to Halve or Double Time of Cure	No. of Reliable Points on Curve	Product of Two Preceding Figures	Av. No. of ° C. to Halve or Double Cure	Temp. Coefficient
					Compound 1											
		142° C.	170° C.						170° C.	185° C.	198° C.					
Time of cure when tensile at 300% elongation equals:	52.8	933.0	58.8	7.1	2	14.2			35.2	..	..	..	..	3	27.6		
					2	14.2	7.1	2.65	52.8	58.8	18.3	7.1	9.2	3	27.6	9.2	2.12
Time of cure when tensile at 400% elongation equals:	105.5	1043	60.8	6.8	2	13.6			88.0	56.5	14.4	5.3	8.3	3	24.9		
	123.2	1293	65.8	6.6	2	13.2			105.5	60.8	19.1	8.6	10.0	3	30.0		
					4	26.8	6.7	2.81	123.2	65.8	..	11.2	11.0	2	22.0		
														8	76.9	9.6	2.06
Time of cure when tensile at 500% elongation equals:	176.0	1123	58.8	6.6	2	13.2			105.5	..	..	..	..	.	....		
					2	13.2	6.6	2.85	140.8	54.4	12.7	4.2	7.6	3	22.8		
									176.0	58.8	18.6	8.3	9.9	3	29.7		
														6	52.5	8.7	2.22
Time of cure when tensile at break equals:	211.3	899	53.6	6.9	2	13.8											
	246.2	1013	57.2	6.7	2	13 4											
					4	27.2	6.8	2.77	211.3	53.6	..	4.5	7.9	2	15.8		
									246.2	57.2	15.3	6.0	8.6	3	25.8		
						Average	6.8	2.77						5	41.6	8.3	2.30
															Average	8.95	2.17

TABLE III. (*Continued*)

Compound 2

Time of cure when tensile at 300% elongation equals:	35.2	760.8	..	...	.	..			35.2	..	12.0	4.4	9.0	2	18.0			
	52.8	928.8	53.6	6.8	2	13.6			52.8	53.6	16.6	6.2	9.0	3	27.0			
					2	13.6	6.8	2.77						5	45.0	9.0	2.16	
Time of cure when tensile at 400% elongation equals:	88.0	882.8	..	...	.	..			88.0	..	15.7	5.3	9.4	2	18.8			
	105.5	970.2	53.6	6.7	2	13.4			105.5	53.6	17.3	6.5	9.2	3	27.6			
	123.2	1052.8	57.1	6.7	2	13.4			123.2	57.1	19.3	8.1	9.9	3	29.7			
					4	26.8	6.7	2.81						8	76.1	9.5	2.07	
Time of cure when tensile at 500% elongation equals:	105.5	712.8	..	...	.	..			105.5	..	12.0	4.3	8.8	2	17.6			
	140.8	850.8	..	...	.	..			140.8	..	14.8	5.4	9.0	2	18.0			
	176.0	1089.8	53.2	6.4	2	12.8			176.0	53.2	17.2	6.8	9.5	3	28.5			
					2	12.8	6.4	2.95						7	64.1	9.16	2.13	
Time of cure when tensile at break equals:	246.2	982.8	53.8	6.7	2	13.4			211.3	..	14.3	5.0	8.6	2	17.2			
	281.7	....	61.5	...	.	..			246.2	53.8	16.3	6.1	9.0	3	27.0			
					2	13.4	6.7	2.81	281.7	61.5	19.5	8.6	9.9	3	29.7			
						Average	6.7	2.81						8	73.9	9.24	2.12	
															Average	9.2	2.12	

TABLE IV. TIME-TEMPERATURE RELATIONS FOR COMPOUND 3

	Value of Property Kg./Sq. Cm.	Seconds to Attain Properties at: 142° C.	170° C.	185° C.	198° C.	° C. to Halve or Double Time of Cure	No. of Reliable Points on Curve	Product of Two Preceding Figures	Av. No. of ° C. to Halve or Double Cure	Temp. Coefficient
Time of cure when tensile at 300% elongation equals:	35.2	...	52.8	18.1	5.6	8.6	3	25.8		
	52.8	...	59.0	19.1	6.1	8.6	3	25.8		
							6	51.6	8.6	2.24
Time of cure when tensile at 400% elongation equals:	88.0	...	51.5	18.3	5.8	8.9	3	26.7		
	105.5	...	54.5	18.8	6.0	8.8	3	26.4		
	123.2	...	59.6	20.3	6.4	8.8	3	26.4		
							9	79.5	8.83	2.19
Time of cure when tensile at 500% elongation equals:	105.5	...	..	17.8	5.0	7.2	2	14.4		
	140.8	537.8	..	18.3	5.5	8.5	3	25.5		
	176.0	586.8	55.3	19.3	6.0	8.5	4	34.0		
							9	73.9	8.21	2.33
Time of cure when tensile at break equals:	211.3	...	59.3	18.9	7.2	9.3	3	27.9		
	246.2	...	63.8	22.5	8.8	9.9	3	29.7		
							6	57.6	9.60	2.06
								Average	8.81	2.20

temperatures to attain the physical characteristics selected as criteria was taken from tensile and modulus curves. From each of these time values the time lag involved in heating up to an active temperature gradient—namely, 7 seconds—was deducted in each case. These corrected data for the compounds are recorded in Tables III and IV. In Figure 9 the time-temperature relation for constant values of modulus at 500 per cent elongation for compound 3 are plotted. From curves such as these which were plotted for the various physical criteria of the three compounds, the corrected time required to attain given physical characteristics was determined at various temperatures.

It was found for compounds 1 and 2 containing 4 and 2.5 per cent of sulfur, based on the rubber content, that the temperature coefficient of vulcanization was not constant over the entire temperature range from 142° to 198° C. Over the range 142° to 170° C. a change in coefficient appears to take place in that a given temperature increment effects decreasing acceleration of cure. However, over the range 170° to 198° C., the temperature coefficient was essentially constant. This may be accounted for on the basis that a slightly larger time correction for establishing a temperature gradient in the rubber should have been applied. For compound 3, containing 1 per cent of sulfur, the temperature coefficient of vulcanization was constant over the entire temperature range.

It appears significant that for the latter compound over the entire range of cures the coefficient is near 2, the value usually associated with organic reactions, and that approximately the same value is obtained for compounds containing larger amounts of sulfur only in the higher temperature range of cures. The apparent change in temperature coefficients found for compounds 1 and 2 in the lower temperature ranges and the absence of change for these compounds in the higher temperature range may be explained on the basis that only the sulfur in solution enters into reaction effecting cure, and that at the higher temperatures of vulcanization there is not sufficient time for the sulfur in excess of the amount in solution to diffuse. As a result, vulcanization is localized. At the lower vulcanization temperatures, however, the time of vulcanization is sufficiently long to allow the sulfur present in excess of saturation to diffuse and accelerate the vulcanization reaction. This would also explain the constant rate of vulcanization found for compound 3 containing 1 per cent of sulfur (based on the rubber) which approximates the solubility of sulfur in rubber at normal temperatures.

The coefficients of vulcanization determined here are given in Table V, together with coefficients found by other investigators and information on the procedures followed.

Although tetramethylthiuram monosulfide alone and in combination with di-*o*-tolylguanidine was used as accelerator in this investigation, several other accelerators and com-

TABLE V. TEMPERATURE COEFFICIENTS OF VULCANIZATION FOR 10° C. TEMPERATURE INCREASE

Literature Reference	Temp. Range, ° C.	% Sulfur, Based on Rubber %	Accelerator	Coefficient	Basis of Determination
(15)	50–75	10	None	2.84	Combined S
(15)	135–155	10	None	2.65	Combined S
(16)	128–168	10	None	2.3–2.6	Physical data
(16)	108–148	10	Organic	2.2–2.5	Physical data
(17)	140–148	10	None	2.4	Physical data
(10)	128–168	10	None	2.3	Combined S
(10)	128–168	10	None	2.3–2.4	Physical data
(10)	108–148	10	Aldehyde + NH_3	2.4	Physical data and combined S
(10)	98–108	10	Aldehyde + NH_3	5	Same
(14)	116.5–166.5	8	15% litharge	2.59	Same
(8)	135.5–162	6.25	None	2.5	Same
(2)	145–171	5	None	2.78–2.88	Physical data
(3)	125–150	4.5	10% litharge	2.45	Vulcanization coefficient of 3
(3)	125–150	4.5	10% litharge	2.2	Physical data
(7)	106–152	3.0	Various organic	1.81–2.00	Physical data
(7)	106–152	3.0	Various organic	1.87–2.11	Vulcanization coefficient
(11)	104.4–154.4	3.0	Two organic	1.92–2.52	Physical data
(11)	104.4–154.4	3.0	Two organic	2.20–2.40	Vulcanization coefficient
(9)	104.4–154.4	3.0	Two organic	1.91–2.32	Physical data
(9)	104.4–154.4	3.0	Two organic	2.30–2.67	Vulcanization coefficient
(4)	110–150	2.5	Various organic	2.0	Physical data
Kemp and Ingmanson	142–170	4	Organic	2.65–3.07	Physical data
	170–198	4	Organic	2.13–2.19	Physical data
	142–170	2.5	Organic	2.65–2.85	Physical data
	170–198	2.5	Organic	2.06–2.24	Physical data
	142–198	1.0	Organic	2.17–2.28	Physical data

binations of accelerators have also been found effective for vulcanizing insulation on wires at 198° C.

Acknowledgment

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A Vulcanization of Rubber Latex by Potassium Ferricyanide*

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The action of iron compounds on rubber, as previously described in the literature, exemplifies the effect of compounds of heavy metals in general—acceleration of oxidation and the breaking down of the rubber macromolecule into simpler units. For example, the presence of very small quantities of iron salts in raw rubber leads to tackiness,[1] and in vulcanized rubber to more rapid aging and deterioration.[2] Various iron compounds act as proöxygens in accelerating the initial absorption of small quantities of oxygen by solid rubber,[3] as well as by benzene solutions of the hydrocarbon,[4] the accompanying degradation in the latter case being immediately apparent by diminution of viscosity. Ferric chloride (in common with halides of other amphoteric metals) has a specific action on rubber, leading to the formation of thermoplastic products at high temperatures.[5] Salts of amphoteric metals have likewise been applied to the treatment of latex, for preparing plastic products which are readily soluble to form solutions of low viscosity.[6]

These various observations of breakdown or depolymerization depend, however, on the oxidation of the hydrocarbon by molecular oxygen. By treating rubber latex with an iron compound in the absence of air, we have found it possible to achieve a quite different action—enhanced polymerization or partial vulcanization of the rubber. The following protocols are illustrative of a large number of experiments in which we have consistently produced a partial vulcanization of latex by potassium ferricyanide, by heating with oxygen excluded.

Terminology.—Natural rubber dissolves only partly in such solvents as benzene or ether, leaving a highly swollen residue which disperses extremely slowly, if at all. Although the terms *sol* and *gel* have been used to designate the soluble and insoluble fractions, respectively,[7] some authors[8] have preferred to consider the proportion of soluble to insoluble rubber simply as related to the average degree of polymerization of the material, which may contain fractions of a wide variety of molecular weights rather than two distinct components *sol* and *gel*.

The term *polymerization* is here employed in its broader sense,[9] to include the existence of cross-linkings between different macromolecules, as well as the linkings between the isoprene units in a single macromolecule. *Degree of polymerization*, in this respect, may be considered as a measure of the total number of linkings per unit volume of material, and *enhanced polymerization* and *depolymerization* as creation or destruction, respectively, of such linkings.[10] Enhanced polymerization of a rubber-like material results in decreased solubility and decreased swelling of the insoluble residual *gel*, and in increased tensile strength; depolymerization, the reverse. In vulcanized rubber, for example, the maximum tensile strength occurs at the same degree of vulcanization as the minimum swelling in solvents.[11] Vulcanization with sulfur may be considered as an enhanced polymerization, without specifying whether the latter is *linear* (increase in length of chain molecules) or *random* (to include cross-linking).

* The results here described are covered by a U. S. Patent application assigned to The B. F. Goodrich Company.

Experimental

Preliminary Observations.—The use of iron compounds as vulcanizing agents was first suggested by the behavior of ammonia-preserved latex concentrate stored in a receptacle of tinned iron. This material developed a pale bluish color after keeping for two months, and the thick coagulum which adhered to the sides of the can acquired a very dark brown color on drying. The latter material had an abnormally high content of ash, considerably more than half of which consisted of ferric oxide (determined by titration with thiocyanate). This iron had been dissolved from the container, perhaps by the action of local couples with the tin coating. Whether it had been in chemical combination with the rubber, or had been adsorbed by the latex particles or precipitated as salts of resin acids, could not be distinguished. In any case, the rubber of high iron content was markedly different in physical character from the rubber obtained from the same latex stored in glass. It resembled, in fact, a lightly vulcanized rubber. This difference is further illustrated by its lower solubility in benzene. The proportion dissolved in benzene in 14 days, and the ash content and iron content, are given in Table I.

TABLE I

DATA FOR RUBBER FROM AN AMMONIA-PRESERVED LATEX CONCENTRATE, STORED IN GLASS AND IN TINNED IRON CONTAINERS

	Ash Content (%)	Iron Content* (Fe_2O_3) (%)	Proportion Soluble in 14 Days
Stored 2 months in glass	0.12	Nil	0.68
Stored 2 months in metal can (body of solution)	0.20	0.064	0.47
Stored 2 months in metal can (periphery of can)	1.15	0.635	0.31

* The average iron content of rubber is given by Dufraisse and Vieillefosse[3] as 0.0025%.

These observations led to a series of experiments attempting vulcanization of latex by compounds of iron. Representative results are presented below.

Material.—All experiments were made with *Hevea* latex buffered at p_H 6.8–7.1 with dilute phosphate buffers. Two supplies of latex were employed. One (*G*) was an ammonia-preserved, centrifuged latex concentrate, furnished through the kindness of The B. F. Goodrich Company. It was purified by dialysis against 0.05 *M* phosphate buffer, and subsequently sterilized according to the procedure of Spence and Van Niel.[12] The other (*E*) had been stabilized with neutral buffer and sterilized immediately after collection in the laboratories of The B. F. Goodrich Company at Kuala Lumpur, F. M. S., and shipped to us in a sterile, sealed container. Some portions of this material, which had never been treated with ammonia, were dialyzed against dilute buffer to remove diffusible serum components, and resterilized to prevent bacterial growth in storage.

Preparation and Testing of Samples.—After treatment of the latex with potassium ferricyanide, as described below, samples were coagulated either by adjusting the p_H to 4.8 with acid, or by pouring the latex on tiles of unglazed porcelain.[13] The rubber was extracted twice with cold acetone and dried *in vacuo*. The degree of vulcanization, or enhanced polymerization, was measured by determining the solubility and degree of swelling. A portion of rubber was immersed in a volume of benzene 100 times its weight. After three days, the solution was decanted from the swollen gel and replaced by its own volume of pure benzene. After fourteen days, this process was repeated. All operations were conducted in the dark room. The swelling of the residual gel was expressed by the *swelling index*, *i. e.*, the volume of gel (cc.) divided by the weight of rubber in it (grams).

Enhanced Polymerization in the Absence of Air.—Samples of latex *G* diluted to

4% rubber content were heated with potassium ferricyanide in air and in bombs sealed under a reduced pressure of nitrogen. The results (Table II) show that, in the absence of air, enhanced polymerization takes place, while heating in the presence of air leads to breakdown, regardless of the presence of ferricyanide.

TABLE II

TREATMENT OF LATEX *G*, 4% RUBBER CONTENT, p_H 7.0

$K_3Fe(CN)_6$ Content (%)	Treatment	Proportion Soluble in 14 Days	Swelling Index
0	Untreated	0.75	120
0	5 hours 100°, absence of air	0.73	110
0.3	5 hours 100°, absence of air	0.22	26
0	5 hours 100°, in air	0.92	..*
0.3	5 hours 100°, in air	0.89	..*

* The amount of residual gel was too small for determination.

Enhanced Polymerization with Various Concentrations of Rubber and of Ferricyanide.—Samples of latex *G* of different rubber contents were heated at 100° in the absence of air with different concentrations of potassium ferricyanide. The solubility and swelling properties of some of the resulting rubbers are summarized in Table III. Enhanced polymerization was evidenced in each case not only by the much decreased solubility and swelling, but also by decreased extensibility and increased toughness in manual testing.

TABLE III

LATEX *G*, p_H 7.0, HEATED AT 100° IN THE ABSENCE OF AIR

Rubber Content (%)	$K_3Fe(CN)_6$ Concn. (%)	Time of Heating (Hrs.)	Proportion Soluble in 14 Days	Swelling Index
		Untreated	0.50	104
4	0.48	5	0.19	32
40	2.0	12	0.28	33
25	2.3	5	0.19	30
25	2.3	16	0.15	22
14	0.14	5	0.28	67
5	0.41	4	0.22	29
5	0.41	18	0.12	23
10	0.39	18	0.12	20
15	0.36	18	0.13	22
20	0.34	18	0.09	22
30	0.30	18	0.18	28

Enhanced Polymerization as a Function of Time: a "Vulcanization Curve."—Samples of latex *G*, of 10% rubber content, p_H 7.0, were heated with 0.15% potassium ferricyanide in the absence of air at 100° for different periods of time. The proportions soluble and swelling indices of the resulting rubbers are plotted in Fig. 1. The lowest values attained are 11% soluble and a swelling index of 23, compared with 46% soluble and a swelling index of 110 in the control.

Effect of Diffusible Serum Components on the Reaction.—The first experiments with undialyzed latex *E* resulted in no enhanced polymerization, but a comparison of undialyzed with dialyzed material showed that this negative result was due to the presence of water-soluble diffusible serum components, and that the inhibiting effect of these could be partly overcome by employing a higher concentration of ferricyanide (Table IV). The color of the latex at the end of treatment is an indication of the amount of ferricyanide remaining, and the lack of any yellow color in the first treated sample suggests that the inhibition here is

the result of complete reduction of ferricyanide to ferrocyanide by the serum components. This is supported by the fact that dilute potassium ferricyanide heated under the same experimental condition with latex serum or with crude quebrachitol (the principal diffusible solute in serum) undergoes reduction to the ferrocyanide. Furthermore, the enhanced polymerization in the treatment of a dialyzed sample can be inhibited by the addition of crude quebrachitol.

Effect of Dispersion.—When a fresh latex coagulum is treated with potassium ferricyanide, the degree of enhanced polymerization is much less than when a fully dispersed latex is treated under the same conditions.

Preservation of Samples.—The first ferricyanide-vulcanized samples tended to age rather rapidly on storage, especially in the light. However, the aging qualities of the vulcanizates were improved by washing out as much of the iron as possible, or by reducing it completely to the ferrous state before coagulation; samples were

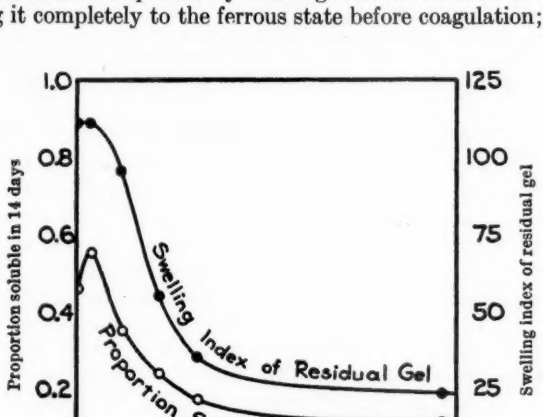

Figure 1

also satisfactorily preserved by adding a small quantity of antioxidant (such as quinol or dimethyl-*p*-phenylenediamine) to the latex before coagulation.

TABLE IV

EFFECT OF DIFFUSIBLE SERUM COMPONENTS ON THE REACTION. LATEX *E*, OF 20% RUBBER CONTENT, HEATED AT 100° IN THE ABSENCE OF AIR

$K_3Fe(CN)_6$ Content (%)	Time of Heating (Hrs.)	Latex	Color after Treatment	Proportion Soluble	Swelling Index
0	Untreated	Undialyzed	..	0.82	90
0.4	18	Undialyzed	White	0.75	88
0.4	15	Dialyzed	Light yellow	0.21	23
1.0	18	Undialyzed	Greenish	0.33	36
1.0	15	Dialyzed	Yellow	0.20	22

Nature of the Reaction

A solution of potassium ferricyanide, heated in the absence of air under conditions similar to those of the experiments with latex, undergoes practically no re-

duction to ferrocyanide. When heated with the serum from a dialyzed latex from which most of the diffusible substances have been removed, only a small amount of ferrocyanide is formed. In the treatment of dialyzed latex itself in the absence of air, however, substantial amounts of ferricyanide are reduced. In amounts up to 1.5% of the rubber (corresponding with one molecule of ferricyanide per 320 isoprene units), its reduction is practically complete after sufficiently prolonged heating, as evidenced by test with ferrous sulfate. This indicates that the ferricyanide actually reacts with the rubber. The overall reaction may involve a dehydrogenation: $2RH + 2Fe(CN)_6''' = RR + 2Fe(CN)_6'''' + 2H^+$, whereby two rubber macromolecules (RH) are joined by a new linking, producing enchanced polymerization. The liberation of hydrogen ion in a buffered system would be consistent with a small decrease in p_H observed in the course of treatment.

In the presence of air, on the other hand, where treatment with potassium ferricyanide leads to breakdown, depolymerization and accelerated absorption of oxygen, the ferricyanide probably serves simply as a catalyst of oxidation of the rubber by molecular oxygen, or as an initiator of reaction chains.[14]

Enhanced Polymerization by Other Metallic Compounds

Several other reducible metal salts were employed in preliminary experiments, heating with latex *G* of 4% rubber content in the absence of air for five hours. With 0.25% of the reagent present in each case, substantially enhanced polymerization was produced by mercuric chloride, ferric chloride, and pentaamminocarbonatocobaltic nitrate. Since potassium ferrocyanide and ferrous sulfate were ineffective, it appears that the metal in its higher valency state is the essential characteristic of the reagent. Its presence in a complex ion, or an undissociated molecule, as in mercuric chloride, probably facilitates reactivity or penetration into the rubber. The ion must be an anion to permit addition to latex on the basic side of the isoelectric point (*i. e.*, p_H 5) without coagulation. (The ferric chloride above mentioned, the multivalent ion of which is positive, was employed in latex adjusted to p_H 3.) A certain instability of the complex ion under the conditions of treatment seems essential, since very stable anions such as those of potassium cobalticyanide, potassium trioxalatochromiate, and potassium mercuric iodide, were ineffective in producing enhanced polymerization, at least under the conditions of our experiments.

Discussion

The production of enhanced polymerization, or vulcanization, of rubber by a compound of a metal hitherto notorious for its deteriorating action is of interest in the light of previous reports of vulcanization of rubber by agents other than sulfur.[15] In the classical experiments of Ostromislensky,[16] for example, vulcanization was achieved by benzoyl peroxide, nitrobenzenes, or ozonized rubber. The effectiveness of these oxidizing agents has been interpreted in several ways, *e. g.*, in terms of the chemical analogy between oxygen and sulfur[17] (an analogy the significance of which is apparently heightened by the fact that selenium also is capable of vulcanizing rubber);[18] as a polymerization catalyzed by peroxide;[19] and, in the case of benzoyl peroxide, as a dehydrogenation similar to that postulated in a preceding paragraph.[20] In any case, the vulcanizing action of these oxidizing agents has seemed inconsistent with the mass of data which demonstrate breakdown and depolymerization of rubber through oxidation. Thus the breakdown of rubber on the mill has been shown to depend on atmospheric oxygen,[21] and to be related to the presence of peroxides,[22] and benzoyl peroxide has been employed to reduce the viscosity of rubber solutions.[23]

These dual roles on the part of benzoyl peroxide and ozone, and now on the part of iron compounds, cannot be regarded as isolated phenomena. Recent work in this laboratory has shown, in fact, that a number of oxidizing agents can build up or break down the polymeric structure of rubber, according to the conditions of treatment. Further examples in this connection will be described in later publications.

Finally, the possibility of alternative polymerization or breakdown by soluble iron compounds, according to whether air is absent or present, suggests another source of some of the variations in physical quality which occur in rubber from latex in the course of its treatment and shipment, since iron is commonly present in commercial latex.[24]

Summary

(1) Vulcanization of rubber is produced by heating latex, from which the diffusible serum components have been removed, with potassium ferricyanide in the absence of air.

(2) In the course of the treatment, the ferricyanide is reduced to ferrocyanide.

(3) A similar effect may be produced by certain other metallic oxidizing agents in the absence of air.

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[17] Cf. Twiss, *Trans. Inst. Rubber Ind.*, **3**, 398 (1928); Fisher and Gray, *Ind. Eng. Chem.*, **20**, 294 (1928).

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[19] Whitby, *Trans. Inst. Rubber Ind.*, **5**, 184 (1929); **6**, 40 (1930).

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[22] Busse, *Ind. Eng. Chem.*, **24**, 140 (1932).

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Rubber in Compression

J. Morrison

Rubber is hardly ever used under simple stresses or strains. A tire tread or conveyor cover is subjected to compression, shear, tension, cutting, and tearing in such a variable and complicated manner that an exact analysis of working conditions is obviously impracticable. Therefore physical tests on samples of rubber will probably never assume the same degree of importance from the point of view of design as in the case of metals, and their primary function will remain that of providing standards for relative comparison of different qualities. Moreover, the comparative value of physical tests is severely handicapped by the variable nature of rubber and by its great deformability, which prevent its being subjected to completely and accurately known stress or strain. Reece (*Trans. Inst. Rubber Ind.*, **11**, 312 (1935)) has pointed out the non-uniform distribution of stress which occurs in tensile testing with dumb-bell test-pieces owing to the necessity for enlarged ends and having to grip the ends and apply the tensile loading initially as a shear through the surface of the test-piece.

In compression testing, the difficulties of securing uniform behavior are much more pronounced. The obvious way to compress rubber is to use a cylindrical test-piece which must be short enough in relation to its diameter to avoid lateral buckling and compress it endwise between parallel plates. Although this does not involve actually gripping the test-piece, the frictional resistance to lateral sliding of the end surfaces on the plates is so great that the rubber deforms to a barrel shape, and the stresses and strains vary in an unknown manner and to such an extent that test-pieces of different sizes behave quite differently.

This difficulty, together with the fact that compression testing does not provide a value for breaking strength, and probably the inference that compressive behavior is in some way a reflection of tensile behavior, is sufficient to account for lack of experimental work done on rubber in compression, and the consequent obscurity of the subject.

Various attempts have been made to overcome end effects in compression testing. Birkett and Drakeley (*Trans. Inst. Rubber Ind.*, **3**, 462 (1927)) first suggested using vaseline on the end surfaces to reduce friction, and by this method the author (*Trans. Inst. Rubber Ind.*, **7**, 112 (1931)) was able to show that the load-deflection diagrams for a range of buffer sizes could be made to coincide for deflections up to about 50 per cent; an empirical method was also indicated by which the load-deflection data for differently shaped buffers in any one quality of rubber could be calculated approximately.

Sheppard and Clapson (*Ind. Eng. Chem.*, **24**, 782 (1932)) have developed an ingenious method of estimating compression data by inflating balloons. The difficulty of preparing balloons accurately and in a wide range of qualities unfortunately limits the usefulness of this technic. Russell (*Trans. Inst. Rubber Ind.*, **9**, 283 (1933)) has proposed a modification of this method by subjecting a flat circular diaphragm to pressure from one side. Thus samples can be easily prepared in various qualities.

Although no claim can be made that compression testing can approach tensile testing in importance, there is an increasing use of rubber in compression as shock-absorbers, engine mountings, seating pads, etc., where the applied loading is rela-

tively simple, and therefore there is a possibility that further work on direct compression testing might be of practical value if the effects of distortion can be even approximately allowed for; moreover such work cannot but add to the available knowledge of rubber.

In the earlier work on various sizes of buffers, it appeared that the compression and tension curves up to 50 per cent strain were almost identical when stresses were referred to actual and not original areas.

In some studies of the stress-strain compression curves, a query was raised whether there was a discontinuity at the zero point. The opinion is generally expressed that the compression and tension curves probably are continuous, but attempts to fit compression curves on to tension curves are not very successful.

To get correlation, one of the curves should be a retraction curve. Also stresses should be expressed per actual area. If they are referred to the constant original area, then the fact that areas are decreasing on one side and increasing on the other will introduce an appearance of discontinuity, although the two methods should both give continuous curves which are tangential at the zero point.

An attempt has been made to draw continuous stress-strain curves through the zero point, the method adopted being to vulcanize a sample of rubber, 0.5 inch in diameter and 0.75 inch long, to two flat-headed brass screws so that it could be either stretched or compressed. A machine was designed to oscillate the rubber by applying tension or compression through a calibrated spring, provided with suitable end caps. The action of turning a handle produced slow oscillations in the rubber-spring assembly, and simultaneously moved a strip of graph paper round a drum mounted parallel to the assembly.

Thus three recording pens attached to the fixed end of the rubber, the rubber-spring coupling, and the driven end of the spring, draw, respectively, a straight line and two oscillation curves, the intercepts representing, respectively, instantaneous values of rubber and spring lengths, from which load and deflection could be calculated. Obviously, the arrangement is incapable of giving true values for stress or strain on account of the distortion introduced by the fixed ends of the rubber, but the error disappears at the zero point, and can be kept small by limiting the amplitude to small strains.

Figure 1 shows typical continuous compression and extension curves for a range from approximately 9 per cent compression to 14 per cent extension. The recorded stresses fell within a range -32 to $+34$ lb. per sq. in. of original area. These oscillations were carried out at approximately 1 cycle per minute, and the figure shown is typical of many.

It would be ridiculous to attempt to draw any quantitative deductions from these diagrams, but in every case a smooth transition from tension to compression or *vice versa* was indicated.

The following experiments on a range of qualities under direct compression were intended to be supplementary to the earlier work on various sizes of test-pieces (Morrison, *loc. cit.*).

Solid cylindrical buffers 1.95 inches in diameter $\times$ 1.645 inches long were prepared of the composition by weight given in Table I.

TABLE I

	A	L	B	C	D	E
Rubber	100	100	100	100	100	100
Sulfur	5	5	5	5	5	5
Litharge	8.5	8.5	8.5	8.5	8.5	8.5
Carbon black	0	10	20	40	60	80

Differences in behavior will arise from the variations in plasticity resulting from the addition on the mill of increasing quantities of carbon black. These differences can be made negligible by masticating the base mix to an extremely low plasticity, but for these experiments it was desired to obtain results which would agree as closely as possible with what would be obtained from production mixings. The procedure adopted, therefore, was to standardize the quantity of rubber on the mill for each batch, and to work each for exactly the time required to make the E mixing, which had the highest black content.

Sheets of each mixing were prepared 0.25 inch thick, from which discs were punched to build up blanks for the mold. Curing was carried out in a small autoclave press for 30 minutes at 40 lbs. pressure.

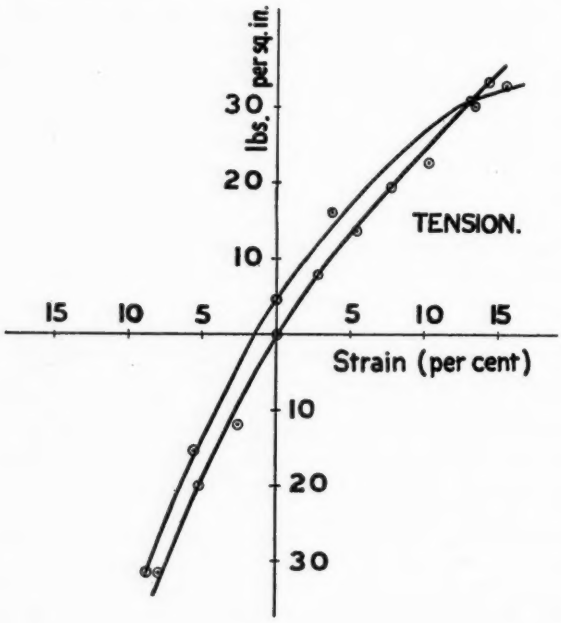

Figure 1

At least 24 hours were allowed between curing and testing. The testing machine used was an Avery 25-ton beam balanced compression tester. Loads could be recorded to 28 lbs. and deflections to 0.01 inch by means of a vernier scale.

It was thought that by making two sets of tests, one between rough and another between smooth lubricated surfaces, two different sets of curves would be obtained, from which it might be possible to draw conclusions regarding the effect of frictional resistance at the ends.

As the actual contact area of a buffer being compressed to a barrel shape is unknown, and as the percentage deflection varies along the length, the curves are presented directly as load-deflection diagrams.

Figure 2 gives the results of tests between metal plates roughed by grooves $^1/_{16}$ inch deep.

As was to be expected, the stiffening by increasing quantities of carbon black is

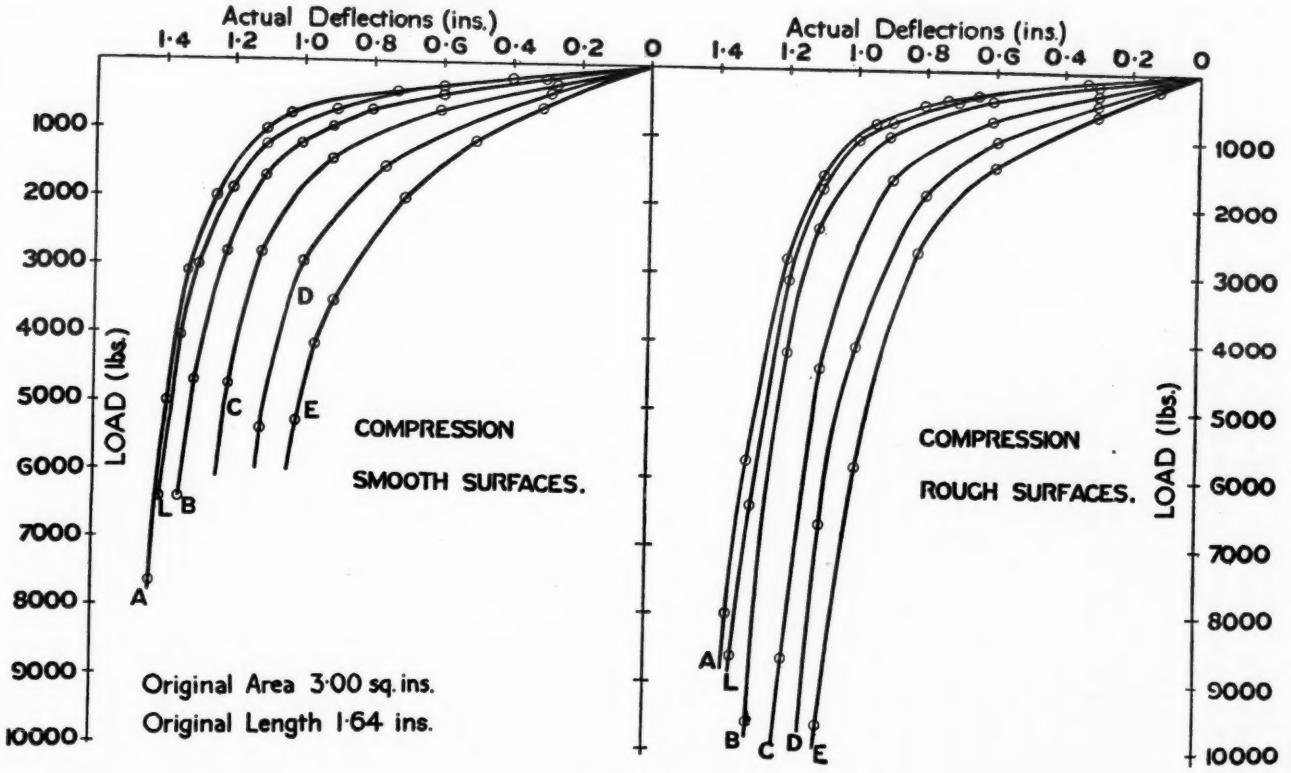
Actual Deflections (ins.)
1·4 1·2 1·0 0·8 0·6 0·4 0·2 0
LOAD (lbs.)
1000 2000 3000 4000 5000 6000 7000 8000 9000 10000
A L B C D E
COMPRESSION
SMOOTH SURFACES.
Original Area 3·00 sq. ins.
Original Length 1·64 ins.
Actual Deflections (ins.)
1·4 1·2 1·0 0·8 0·6 0·4 0·2 0
LOAD (lbs.)
1000 2000 3000 4000 5000 6000 7000 8000 9000 10000
A L B C D E
COMPRESSION
ROUGH SURFACES.

Figure 2

indicated in a similar manner to the curves already published for tension. Buffers A, L, B, and C failed by splitting circumferentially around the middle of the bulge where the indirectly induced tension was highest, and on release showed a distortion to the shape indicated in Fig. 3.

Figure 2 also shows the corresponding curves when compression is carried out between plate-glass surfaces lubricated with a light grease.

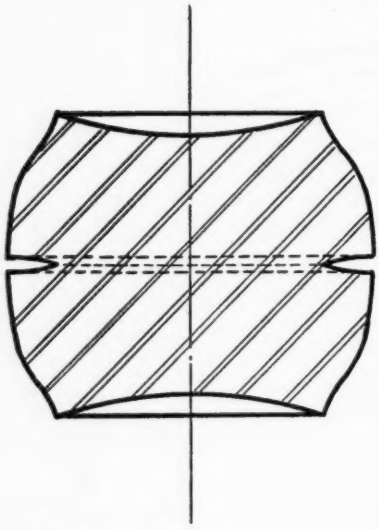

Figure 3

The main difference between the two sets of curves lies in an increased spread caused by lubrication. This is most noticeable at high loadings. The curve for the heavily compounded mix E is least affected, the others being displaced to the left, indicating less stiffness, by increasing amounts. This shows that compound E was already slipping on the roughened plates, and this was confirmed by the marking left on the ends of the buffers by the compressing surfaces. For mixings A, L, and B, the marking is a clear impression of the grooving on the plates, but for the harder mixings it is blurred and covered by radial lines, indicating that slipping has taken place. It could be observed also during the test that the barrelling was greatest with the softest quality, and that it was still quite appreciable with each quality when using the lubricated glass plates.

As was to be anticipated, therefore, the data given by these tests are influenced to an unknown extent by the amount of sliding which has taken place. Obviously, this was an unsatisfactory position, and it was becoming increasingly doubtful whether any useful information could be extracted from these curves.

Apart from reverting to some alternative and more artificial method of testing, only one course remains open, that is, to estimate as far as possible where the curves ought to be and compare with the actual positions.

The effect of increasing quantities of carbon black on rubber has been studied in detail in tension, generally in terms of the increased resilient energy obtained, and it was thought that this tensile knowledge might be useful in an analysis of compression curves. This energy increase or reinforcement is usually obtained by deducting the resilient energy per unit volume of the uncompounded base mix at a given elongation from that of the compound at the same elongation. Lunn (*Trans. Inst. Rubber Ind.*, **4**, 396 (1929)) applied a correction to take account of the reduced amount of base in unit volume of compound. The author wishes to draw attention to a further correction which can be made, and which will account for some of the apparent reinforcing property of carbon black.

It seems reasonable to suppose that when a mixture of carbon black and rubber is elongated or compressed, the strain must take place mainly in the rubber, the carbon particles remaining rigid. It follows, therefore, that, if 1 inch of rubber and 1 inch of mixture be both strained by x per cent, as there is less rubber in the mixture the strain must be greater than x per cent. A comparison of resilient

energies at constant elongation includes a stiffening effect which arises simply from dilution, and does not depend on any physical attributes of the carbon black or other pigment, such as specific surface.

Consider a very thin length cut from any part of a test-piece in a quality containing 100 volumes of base and V volumes of carbon black. The diameter of this elementary rod is supposed to be small in relation to the diameter of the carbon black particles. Its length is made up of lengths of base and lengths of carbon black which, multiplied by the area of the elementary strip, will give volumes of base and volumes of carbon. If the distribution is perfect the ratio of these volumes, and therefore of the lengths, will be equal to the total ratio of base to carbon, *i. e.:*

$$\frac{\text{Length of rubber in compound}}{\text{Length of compound}} = \frac{100}{100 + V}$$

The same result can be obtained by considering a cube of compound of total volume $(100 + V)$, and supposing that the black particles are caused to disappear and the resulting cavities in the remaining cube of rubber closed up by a contraction of length at constant area. The length of the original cube of compound is $(100 + V)^{1/3}$ and the contracted length will be:

$$\frac{\text{Rubber volume}}{\text{Area}} = \frac{100}{(100 + V)^{2/3}}$$

Hence

$$\frac{\text{Length of rubber in compound}}{\text{Length of compound}} = \frac{100}{(100 + V)}.$$

For any extension or compression of the compound the

$$\frac{\text{Strain in the rubber of the compound}}{\text{Strain in the compound}} = \frac{100 + V}{100}.$$

This extremely simple relation for the stiffening action of pigment loading can be criticized severely. It ignores completely the shape of the rubber element associated with each pigment particle and any surface effects at the rubber-pigment interface.

The justification for its inclusion here lies entirely in the contention that, even if inaccurate, it is a move in the right direction, and in the fact it did help to show up more clearly one feature of the distortion in compressing rubber.

Table II shows the correction applied to breaking elongations given by Barron and Cotton (*Trans. Inst. Rubber Ind.*, **7**, 209 (1931)).

TABLE II

Carbon black	0	1.3	5.5	8	11	16	23	34
Total volume	109.5	110.8	115	117.5	121.5	125.5	132.5	143.5
Total ratios	1	1.01	1.05	1.07	1.11	1.14	1.21	1.31
Elongation at break	770	750	703	690	660	650	640	500
Elongation corrected	770	757	740	738	726	742	774	655

Table III gives the results from Schopper ring tests on the range of qualities used for these compression tests.

TABLE III

	A	L	B	C	D	E
Carbon black	0	5.16	10.33	20.67	31.01	41.35
Volume ratios	1	1.05	1.1	1.2	1.3	1.4
Elongation at break	850	645	632	557	444	265
Elongation corrected	850	677	695	645	577	371

The volume ratio-correction tends to reduce the drop in elongation caused by increased loading of carbon black, but as was to be expected, the correction is quite incapable of giving a complete equalization. It was thought worth while,

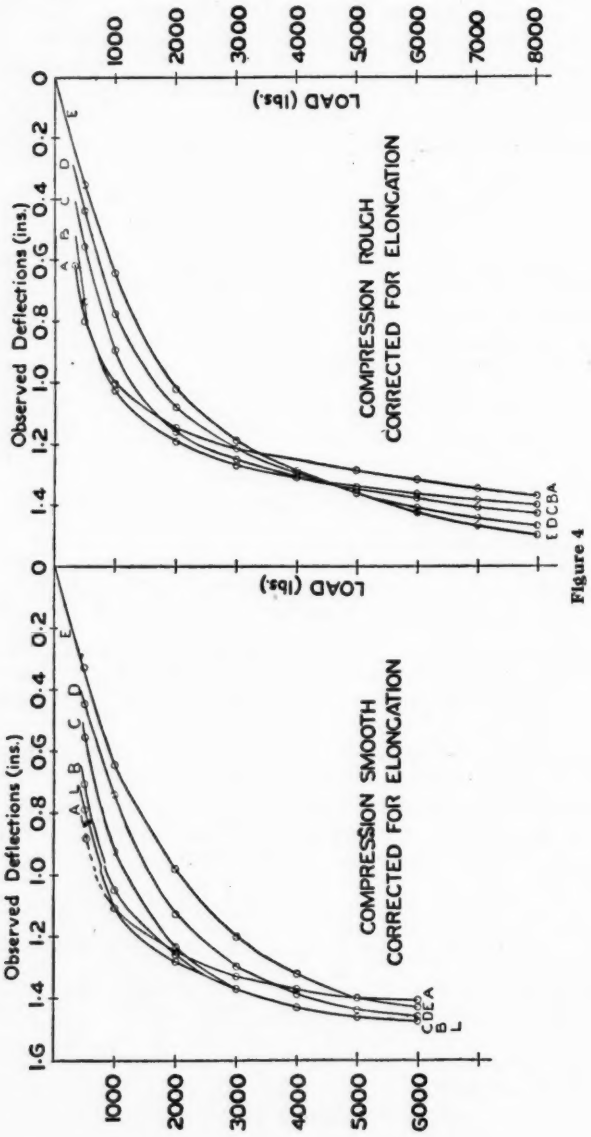

Figure 4

however, to apply the correction throughout the load-deflection curves of Fig. 2 to see whether better results could be obtained at low strains. That this is not the case is shown by Fig. 4. The correction factor succeeds in very considerably re-

ducing the spread of the curves at large deformations, but has much less effect nearer the origin.

These curves now show a rather unexpected feature. They change over so that the softer qualities are offering the greater resistance. This may be due simply to error in the correction factor, but it can be explained on the grounds of non-uniform strain. For the softer qualities more "barrelling" takes place, and higher indirect tensile stresses are set up, and these indirect stresses eventually outweigh in a sense

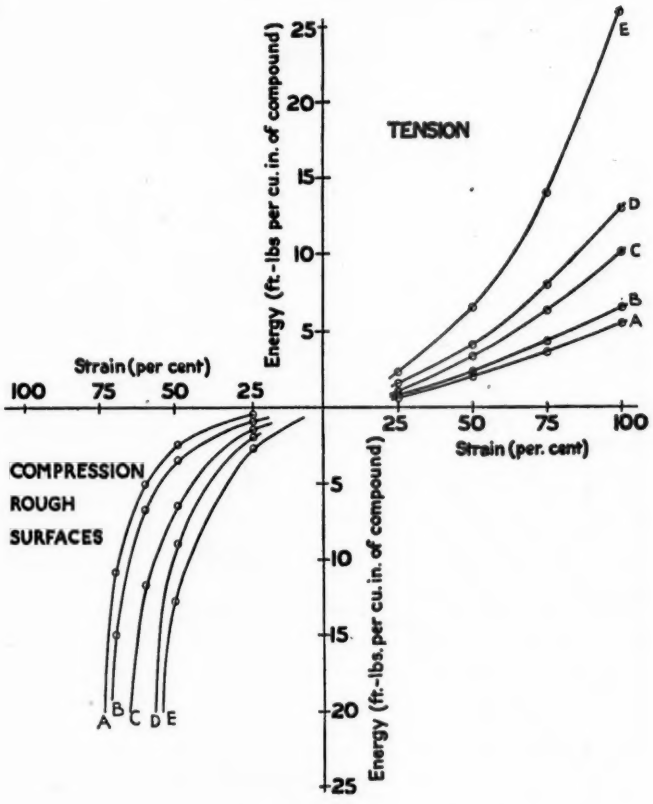

Figure 5

the compressive stresses and cause the softer qualities to offer a relatively greater resistance to further deformation.

The curves for the rough surfaces all cross each other at the same point, with the exception of the base. This is not considered to have any special significance. A repeat experiment would probably show the curves crossing each other consecutively. On lubricated surfaces the rearrangement is not so well marked, but the tendency to reverse the order is clear. E is, however, still in the second place. An extension of the curves to higher stresses would no doubt bring E further over, but in general the spread of the curves at these high stresses is reduced to an amount which could be accounted for by experimental error, or variations in the mixings other than by the simple addition of carbon black.

It should be noticed that the disproportionate softness of the base A, as indicated in Table II, is reflected by its increased stiffness in Fig. 4.

Obviously the elongation correction completely fails to provide any degree of correlation between the curves for the range of compression under which rubber is

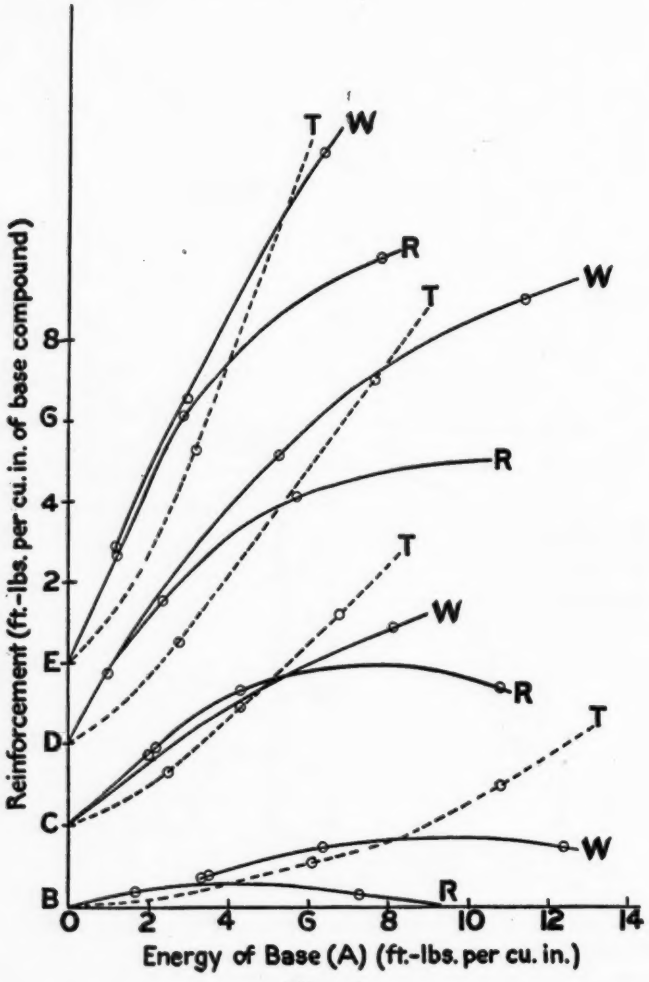

Figure 6

used, and until further investigation improves the position, the behavior of a range of qualities in compression cannot be expressed as a simple function of the composition.

The distortion undergone by rubber in compression is clearly very different from that which occurs in tension, and it might be of interest to see how far this difference is reflected in the energy curves.

Tests were accordingly carried out on the same range of qualities in tension, using a Nesbitt pendulum machine, with which the loading could be applied by hand. An interval of approximately 30 seconds was allowed after each increment of extension before readings were taken, thus giving a rate of loading comparable with the compression tests.

A dumb-bell test-piece was used, having a restricted area of 0.023 sq. in. for a length of 1.25 inches. Extensions were measured by bench marks 0.25 inch apart at the center. Areas were measured from the load extension diagrams by planimeter, and energy values in ft.-lb. per cubic inch of compound were calculated. The curves connecting energy with overall percentage strain for both tension and compression are shown together on Fig. 5.

The curve for compound L has been omitted on account of the small differences between it and A or B. Corresponding curves in opposite quarters fit together better than was expected. They approach zero with the same slope and for low deformations are approximately linear, which agrees with the results obtained by reciprocating the small sample as shown in Fig. 1.

The difference between tension and compression is more clearly shown by the energy difference or reinforcement curves on Fig. 6. These differences were calculated by adjusting the energy values for the compound to the appropriate amount of base in the compound and deducting from that the energy of base taken direct from the A curve at an elongation adjusted in accordance with the correction already described.

To obtain a comparison it is obviously no longer reasonable to use the percentage strain as abscissa, and therefore energy differences have been plotted as a function of the resilient energy (or total energy of deformation) of the base, *i. e.*, the base energy which was deducted to obtain the differences.

For convenience these curves for tension T, compression on lubricated surfaces W, and on rough surfaces R, are grouped for each compound.

It will be noticed that reinforcement in tension tends to have a linear relation to resilience for the low tensile strains under consideration (under 300 per cent). Reinforcement in compression is initially higher than in tension, and then falls off to lower values fairly rapidly, again indicating the stiffening effect which arises from the greater distortion of softer compounds. The lubricated compression curves show more reinforcement than those for rough surfaces, indicating the extent to which lubrication has reduced the differences in distortion.

These reinforcement curves are included simply as a matter of interest. They serve to show how seriously the behavior of rubber is influenced by the extent to which stresses and strains are not uniform, and emphasize the difficulty of obtaining fundamentally accurate or consistent results, owing to the lack of method of subjecting rubber to a uniform and precisely known deformation.

The main purpose of these experiments was the essentially practical one of investigating the possibility of deriving a formula which would indicate the amount of pigment to be added to a particular type of compound in order to produce a given behavior in compression. Obviously such a formula will at present have to be entirely empirical and be rigidly limited in application Probably the most convenient form would be an alignment chart connecting deflection, stress and pigment loading, applicable up to about 50 per cent overall deflection.

The author wishes to gratefully acknowledge the assistance received from the heads and staffs of the laboratory, mixing, molding, and engineering departments of the Leyland and Birmingham Rubber Co., Ltd.

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The Brittleness of Ebonite

R. Ariano

Introduction

In an earlier publication (*La durezza Brinell per i metalli, per la gomma e per l'ebanite, L'Industria*, 1929) is to be found information of a purely general nature on the behavior of ebonite from the point of view of brittleness. Since this subject has considerable practical interest, it seems desirable at this time to examine the subject in more detail.

As with metals, the brittleness of ebonite can be estimated by measuring the "resilience" or the unit work of fracture by bending a small bar of ebonite supported at each end and subjected to impact. The greater the brittleness, the lower is the resilience measured in this way.

Metals are fractured in the form of small bars with suitable notches, and many investigations have been devoted to this subject and to standardization of the form, dimensions, and preparation of test-specimens. In spite of this, no general unification of technic has yet been attained. The reason for a notched test-specimen is obviously to localize the stresses and strains to a restricted section.

The question then arises, is the same technic suitable for ebonite? It was shown in the earlier work cited above, and several examples were given in support of the contention, that a notch lowers the resilience (the sharper this change in contour, the greater this effect), though of course this effect is of only relative significance. The real problem is therefore whether a notch increases the sensitivity of the brittleness test. The question may also be asked whether small fissures have any marked effect on the brittleness of a material. *A priori*, the resilience of metals is of the order of several kilograms per sq. cm., that of ebonite is only about one-hundredth of this value. In other words, ebonite is about one hundred times as brittle as iron. The properties of ebonite are therefore such that it is doubtful whether the stresses need be localized.

The Technic of Testing

The apparatus used in the testing was a Schopper pendulum machine, with impact beam having a round head (ϕ = 2.5 mm.). The maximum work with the particular beam employed was 40 cm.-kg.

The test-pieces were cut out by a press, using a multiple die, both for smooth specimens and for notched specimens, so that the average resistance of test-specimens could be determined. The length of the specimens was in all cases 120 mm.; the cross sections shown for the individual cases were measured after the vulcanized specimens had been polished with emery cloth on all their faces to make them smooth, and parallel and perpendicular to each other where rectangular specimens were concerned. Cylindrical test-specimens were turned on a lathe. The forms of the test-specimens and of the supports, and the meaning of the symbols, are indicated on the diagrams which follow.

Appearance of the Fractured Section and the Conclusions Which May Be Drawn

Commencing with the surface which receives the impact, there appears a zone which is almost lustrous, indicating that fracture is sudden. Furthermore in this

zone there are protuberances, cavities, and vacancies where pieces have become detached. On the other hand the remaining section is generally composed of a compact surface on which the destruction of the fibres is visible. It is evident therefore that there is a distinct difference between the work expended on the first fibres which undergo the impact and the remaining fibres. Only a small section of the test-specimen is subjected to actual impact, while the remainder of the specimen undergoes rapid, though not instantaneous, flexure.

To demonstrate this, photographs of fractured sections of rectangular and also round test-specimens without notches are shown in Fig. 1. Two vulcanizates were included, and these will hereafter be designated as *ebonite* and *Diamantite*. The ebonite was prepared from the classic mixture of 68 parts of rubber and 32 parts of sulfur, with the addition of a little dust of the same ebonite. Diamantite was a commercial hard rubber containing a considerable loading.

The test-specimens shown in the photographs were all vulcanized in the same way, *viz.*, all ebonite samples for 80 minutes at a steam pressure of 7 atmospheres, and all Diamantite samples for 120 minutes at a steam pressure of 4 atmospheres; in all cases in a press. All were fractured with a force of 40 cm.-kg.

It is evident that the Diamantite was more fragile than ebonite. Figure 1, in fact Fig. 2 as well, show that the fractured sections of ebonite undergo more disruption than do those of Diamantite. As may be seen in Fig. 1, the zone which fractures first is in every case a restricted area; and it may be assumed that its share in the energy of fracture is relatively small.

It will be observed also that the smaller the moment of inertia, the less is the damage at the fractured section. Thus the round specimen of Diamantite, having $\phi = 9$ mm., showed a fairly smooth fractured section. In the case of ebonite test-specimens having $l = 10$ and $p = 15$, there is evident in one case (the first specimen at the left) a fractured surface which is almost spherical and is very smooth. This is due to the fact that the impact has broken the specimen into three pieces (the small middle one of which was lost and therefore was not photographed).

All this indicates that the test-specimen, like metals, does not react as a unit, even within the section; in other words we are not concerned with the measurement of a well-defined physical property.

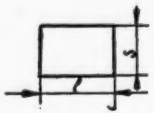
In our present state of knowledge of the subject, the test must be accepted as only a comparative one, in which the dimensions and the shape of the test-specimen, the dimensions of the impact beam, etc., are in process of being defined exactly and, if possible, standardized internationally (a German standard has already been adopted).

Since the part affected by the initial impact is relatively small compared to the whole section (10×15 cm. in the test-specimens concerned), one would naturally expect that the smaller the test-specimen the more nearly it would react as a single unit, and the less its resilience; the larger the test-specimen the more closely would the test approach a rapid stress rather than a sudden shock, and therefore the greater is the resilience and the less irregular its values. Furthermore the greater is the effective force of the striking beam at the instant of collision, the more localized is the deformation and therefore the more sensitive is the test (cf. the earlier work for the difference between the results with a force of 10 kg.-cm. and one of 40 kg.-cm.). The facts described are applicable to smooth test-specimens at equal states of cure.

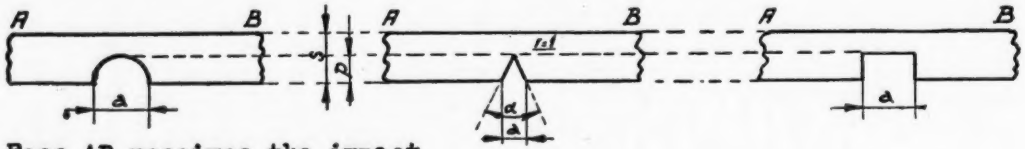
Examination of the test-specimens shown in the lower part of Fig. 2 (the times of vulcanization are given in the figure) seems to justify the conclusion that the time of vulcanization, at least for ebonite, has a marked influence on the appearance of the fractured section. Damage to the zone which is not broken directly by im-

Types of Specimens Tested

Circular test-specimen, ϕ mm. diameter

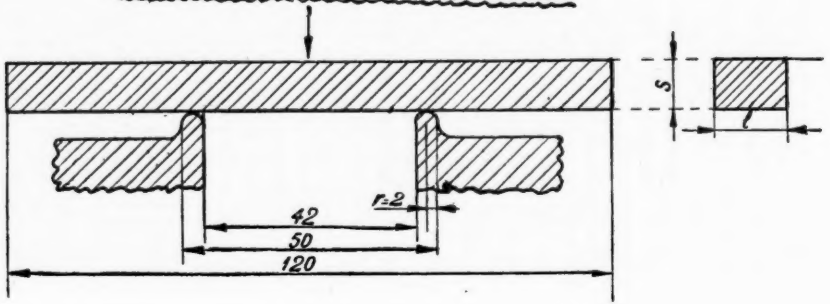


Rectangular test-specimen { l = width (transverse dimension receiving the impact)
s = thickness (transverse dimension perpendicular to l)



Face AB receives the impact

Arrangement of Test-Specimen



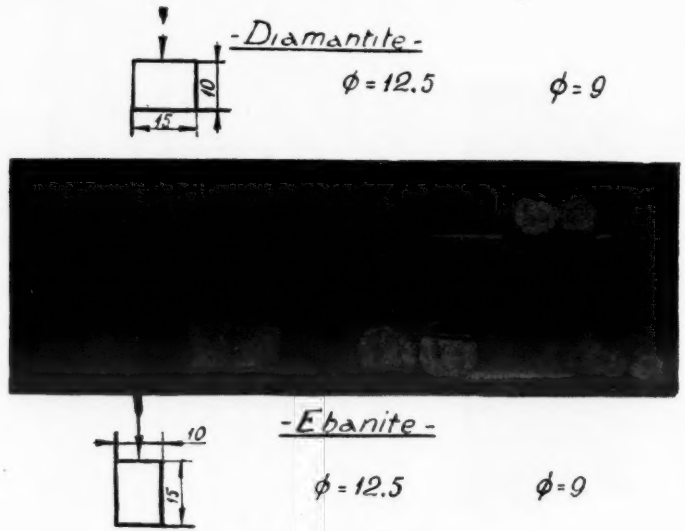


Figure 1

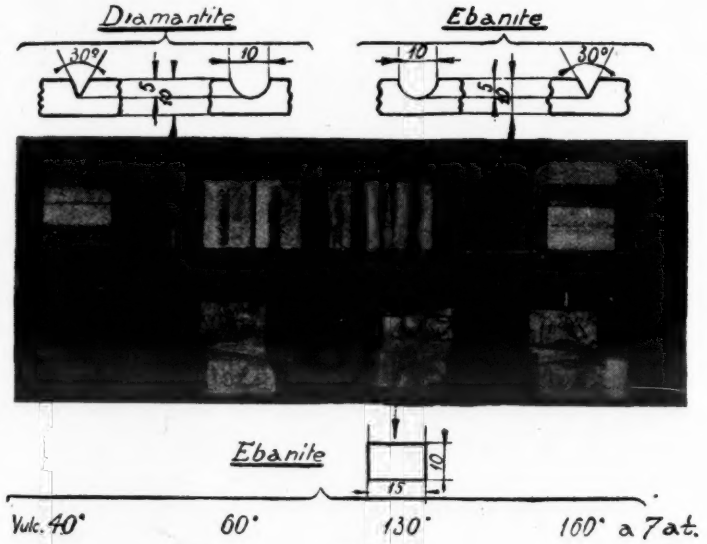


Figure 2

pact seems to become greater with increase in the time of vulcanization to a point where there is no longer any change, at least a perceptible one.

It has already been shown that with change in the composition of the mixture, the structure of the fractured section changes. It should be added that variations quite independent of unusual conditions may occur in different lots of the same ebonite manufactured in the same factory, as a result of differences in processing, differences in vulcanization, etc. An idea of this may be had in Fig. 3, which shows fractured sections of two series of test-specimens prepared from two different mixtures. At the side of each test-specimen is shown the resilience (in kg.-cm. per sq. cm.) and also the hardness (Δ the ratio of the load, 50 kg., exerted by a small steel ball of 10 mm. diameter, to the area in sq. mm. of the impression, which is assumed to be spherical, and is calculated from the stem of the instrument). These average values were obtained at several points of the test-specimens, and were measured on two specimens obtained by impact fracture.

Although it cannot be accepted as a general fact, these fractures seem to indicate that, even when the resilience remains the same, the structure may vary with variation in the hardness.

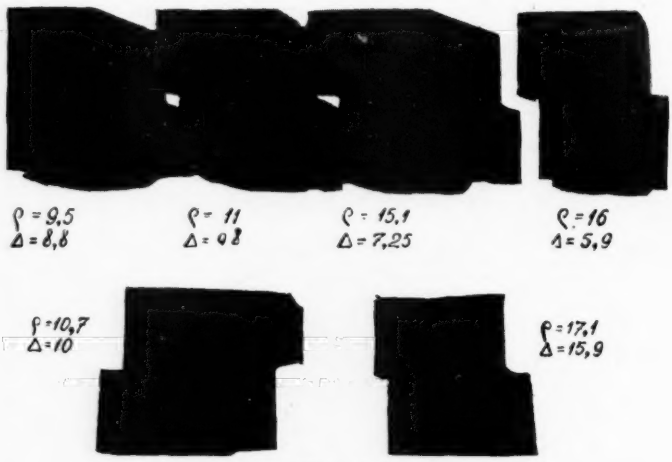


Figure 3

Figure 2 shows the appearance of fractured sections of notched test-specimens. The shapes and dimensions of the notches are recorded above the test-specimens. A comparison with fractures of the corresponding specimens without notches, in Fig. 1, shows that notching diminished the difference between the appearance of the zone of initial impact and the remainder of the section, though the difference was still appreciable. Moreover, these notched specimens showed the same general behavior described for specimens without notches.

The first observation explains the low resiliences of notched specimens compared with specimens without notches, even when the two had the same moments of inertia at the minimum cross sections. (It will be shown below that this is true in practice.)

Experimental Results

Influence of the Time of Vulcanization.—The data shown in Fig. 4 indicate that a brittleness test is adapted to ascertaining differences in states of vulcanization only

for undervulcanized samples. The state of vulcanization considered from the practical point of view as the optimum (80 minutes at 7 atmospheres for the mixture concerned) corresponds to the beginning of the period where the resilience varies but little with the time of vulcanization. This was found to be true of both the smooth test-specimens and the notched specimens which were tested. The practical insensitivity to excessive vulcanization, at least over a wide range, was indicated in the preceding discussion dealing with the appearance of the fractured sections.

Influence of the Moment of Inertia of Impacted Sections.—Figure 5 shows that, as would seem logical, the moment of inertia is the principal geometric factor which controls the resilience. Nevertheless a careful examination will show that it is not the only factor. For example, the data in the preceding figure would seem to indi-

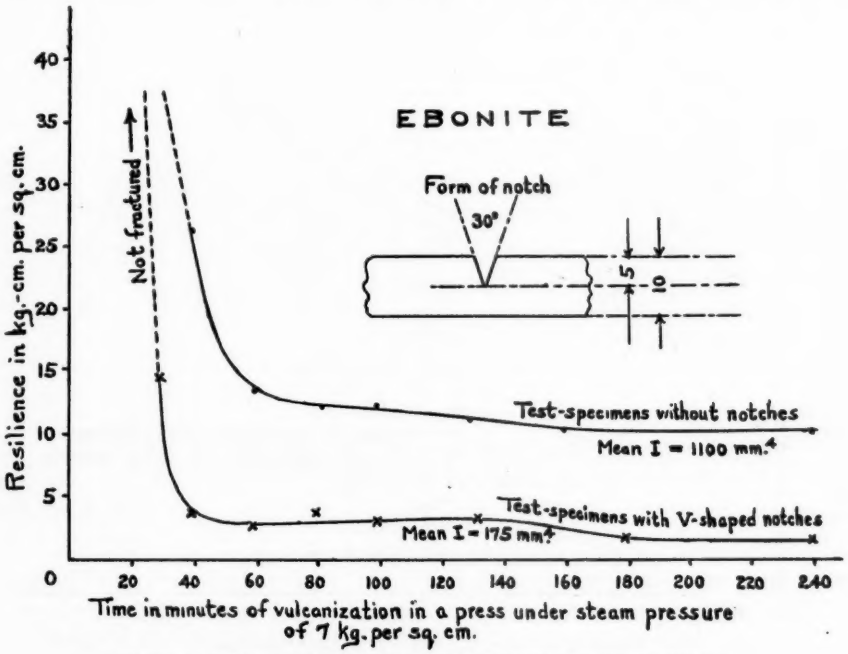


Figure 4—Influence of the Time of Vulcanization on the Resilience

cate that the form of the section itself is of considerable importance. Round and square sections in particular seem to give higher resilience values than the corresponding rectangular sections (in the case of sections which are not notched). More extensive experimentation would be necessary before any definite laws might be derived. However, Fig. 5 shows clearly that there is no simple proportionality between moment of inertia and resilience. This also confirms what is evidently a universal law, *viz.*, that within a restricted range linear relations are approached; in the present work this is especially true of sufficiently high values of the moment of inertia, *e. g.*, above 600 mm.⁴

Influence of the Type of Mixture.—Figure 5 also shows clearly that at the optimum cure, even with the same moment of inertia and form of test-specimens, the resilience reveals the influence of the composition of the mixture, *e. g.*, the

resilience of ebonite is higher than that of Diamantite; in other words, ebonite is less brittle than Diamantite. Naturally in construction problems, it is of particular importance to study the brittleness of ebonite to be certain that this property is satisfactory for the purpose. It might be added that differences caused by different times of vulcanization can be minimized by the proper choice of mixture; however, this is of comparatively little interest because the range of practical insensitivity to further vulcanization is sufficiently great.

Influence of the Notch and Its Form.—As is already known (cf. the earlier cited work of the author) a notch in a test-specimen lowers the resilience. It is evident

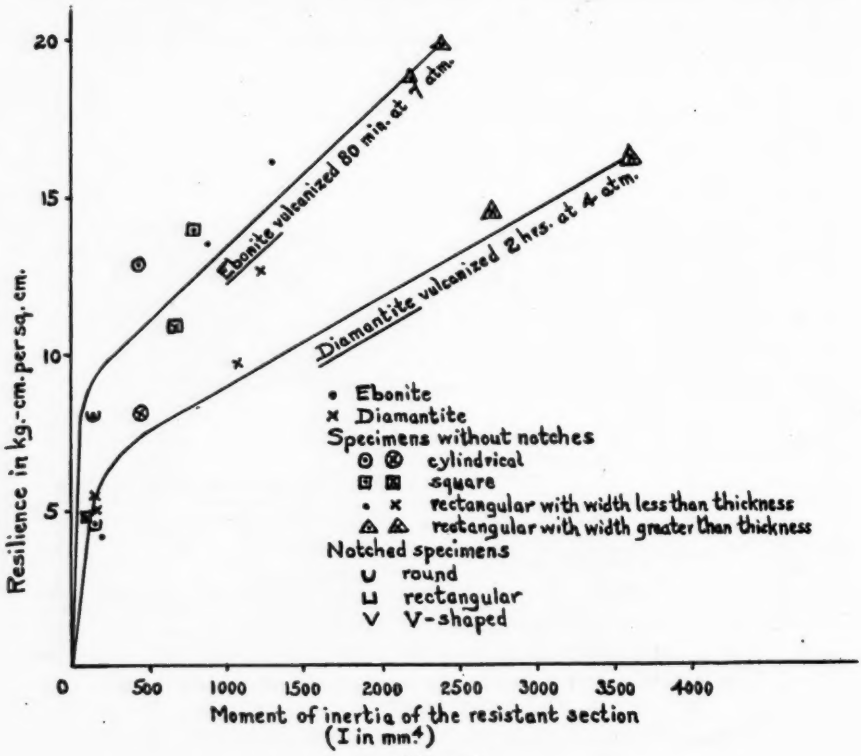


Figure 5

from Fig. 4 that with a V-shaped notch, the depth of which reaches one-half the thickness of the specimen, the resilience is reduced to about one-eighth its value for the corresponding smooth specimen. It might be thought that this is attributable to the notch diminishing the moment of inertia of the fractured section. As a matter of fact, however, it was confirmed that for a given moment of inertia there is no appreciable difference between the resilience of smooth test-specimens and notched (round, rectangular, and V-shaped with a depth one-half the thickness) specimens of Diamantite. On the other hand, with ebonite, the presence of a notch, as shown in Fig. 5, is evident in the results, even with equal moments of inertia of the fractured section. Not only is this so, but also the form of the notch is seen to play its part, in the sense that for a given moment of inertia the resilience

is highest with no notch, is less with a round notch, is still less with a rectangular notch, and is least with a V-shaped notch. This means that the more brittle is the material tested, the less is the influence of the notch. Nevertheless, as is evident by an examination of Fig. 4, differences in the state of vulcanization even of ebonite are no more evident with notched test-specimens than they are with smooth specimens.

Influence of the Dimensions of the Notch.—With a given type of notch, it would seem logical to expect a gradual change in resilience with change in the depth of the notch, and also with a change in the moment of inertia. The table which follows summarizes the average results of tests of specimens having V-shaped notches in comparison with the results of tests of specimens without notches. In each case the specimens were ebonite vulcanized for 80 minutes at 7 atmospheres' pressure.

TABLE I

No. of Sample	Dimension a (Mm.)	Dimension b (Mm.)	Angle α (Degrees)	Moment of Inertia I_4 (Mm.)	Resilience, ρ
1	0.8	2.4	30	15.7	1.42
2	0.9	4.2	30	92.4	1.78
3	0.85	5.6	30	218.	1.89
4	0.85	8.2	30	670.	2.15
5	1.2	6.5	30	334.	2.06
6	1.2	8.3	30	692.	2.4
7	3.	6.5	30	342.	2.52
8	3.6	4.5	30	112.	2.72
9	4.4	3.	30	33.2	3.82
10	4.3	5.5	30	200.	4.12
11	5.7	3.4	8	47.6	3.67
12	1.4	7.3	85	472.	2.84
13	0.	5.	..	154.	10.3
14	0.	10.	..	1100.	12.3

This table indicates clearly four facts.

(1) There is a sharp increase in resilience in changing from smooth unnotched specimens to notched specimens. This means that a notch, even when not at all deep, brings about a considerable diminution in resilience (in the table compare nos. 1–4 with 13–14).

(2) For a given depth of notch, changes in the resistant thickness ($b = s\text{-}p$), and consequent changes in the moment of inertia, result in similar but much smaller changes in the resilience. Thus in passing from no. 1 to no. 4, the resistant thickness changes from 1 to 3.4, the moment of inertia from 1 to 43, the resilience only from 1 to 1.5.

(3) For a given resistant thickness (b), the resilience diminishes with increase in the depth of the notch, and therefore with diminution in the moment of inertia, but this diminution in resilience is proportionally much less than the increase in depth of the notch. For example, with no. 4 and no. 6:

$$\frac{a_6}{a_4} = 1.4 \sim \qquad \frac{I_6}{I_4} = 1 \sim \qquad \frac{\rho_6}{\rho_4} = 1.1$$

and with no. 5 and no. 7:

$$\frac{a_7}{a_5} = 2.5 \qquad \frac{I_7}{I_5} = 1.02 \qquad \frac{\rho_7}{\rho_5} = 1.2 \sim$$

(4) The angle of aperture of the notch has an enormous influence. Thus with no. 11, the minimum angle of aperture (no. 8) shows a distinctly higher resilience than does no. 12, in fact $I_{12} = 10\, I_{11}$.

Finally then it may be concluded that a small notch is sufficient to cause a considerable diminution in resilience, and that if any standardization is to be attempted, it will be necessary, if a V-shaped notch is adopted, to define carefully the dimensions of the test-specimen and notch, and above all to define in a precise manner the angle of aperture of a V-shaped notch.

Summary

The results of tests of the brittleness of ebonite are described.

Resilience is influenced chiefly by the moment of inertia of the cross section of the test-specimen, but it seems also to be affected by the form of the specimen.

The state of vulcanization has considerable influence on these mechanical properties within the undercured range, but with thorough vulcanization the state of cure plays no appreciable part.

Notching of test-specimens is not of great importance. It diminishes the resilience, but when the tests are compared on a basis of equal moments of inertia of the resistant cross sections, this diminution becomes inappreciable in the case of brittle ebonites. On the other hand, the shape of the notch in ebonites containing no loading ingredients does influence the resilience.

With V-shaped notches, the depth of the notch and its angle of aperture influence considerably the resilience of this latter type of ebonite, and notches of minimum depth are sufficient to have an appreciable effect.

[Translated for Rubber Chemistry and Technology by K. Kitsuta from the Journal of the Society the Rubber Industry, Japan, Vol. 9, No. 11, pages 555–561, November, 1936.]

Studies of Hard Rubber Reactions

III. Changes in Acetone-Extractable Substances during Vulcanization*

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In the preceding experiments (cf. *J. Soc. Chem. Ind., Japan*, **39**, Suppl. binding, 76–79, 100–101 (1936)), the author studied the reactions which take place during the formation of hard rubber by following the physical characteristics, such as tensile strength, elongation, and hardness of vulcanized soft and hard rubbers containing diphenylguanidine as accelerator. The present experiments include tests of the chemical properties of hard rubber. The tests of the physical and chemical properties may throw light on the fundamental principle of the hard rubber reaction.

There has been practically no systematic investigation of the changes in acetone-soluble substances during vulcanization, and only a few scattered studies are to be found in the literature. For example, Weber[1] states that the acetone extract after vulcanization is 3 to 5 per cent higher than the content of resinous substances in the raw rubber, while an entirely different experimental result was obtained by Ditmar and Wagner.[2] According to them, the acetone-soluble substances decrease during vulcanization because rubber and resinous substances vulcanize at the same time and change into acetone-insoluble substances. Besides, some have reported decreases in acetone-soluble substances during the vulcanization of soft rubber, including Fol and Heurn,[3] Feuchter,[4] Minatoya and Aoe,[5] and Hada,[6] but definite conclusions regarding changes in acetone extract during vulcanization cannot be drawn from these publications.

I. Preliminary Experiments on Acetone Extraction

Samples were vulcanized in the same way as described in the first Communication. Soft rubber samples were passed several times through a cold laboratory mill, creped to less than 1 mm. thick, and cut into strings with scissors. Hard rubber samples were ground into powder by passing through an alundum grinder and sifting through a 100-mesh sieve. Samples of 0.5–1.0 gram were used for the tests.

An extractor was designed of the same general type as the Cottol apparatus in which extraction is carried out by suspending the syphon cup in acetone vapor. The system is connected by a ground glass joint to the condenser, which is a vertical tube with bulbs. The condensed acetone does not drop directly on the syphon cup, but it is collected in a receiver, from which the distillate can be removed. Here the acetone is warmed before dropping.

There are considerable differences as to the correct time for extraction. For instance, Experimental Method No. 1 of the Rubber Society of Japan[7] sets the time of acetone extraction of hard rubber over 48 hours, while the British Standard Specifications[8] recommend only 8 hours of continuous extraction. Other times are recommended, for instance Weber[9] recommended 72 hours for hard rubber, and Caspari[10] 20 hours. In short, these times have been chosen for convenience or as necessary for products differing in conditions of preparation or different in their uses, and there seems to be no ideal time of extraction for all kinds of hard rubber.

* This article appeared in shorter form in Rubber Chem. Tech., **10**, 153 (January, 1937).

It is also difficult to set a definite time as the type and efficiency of extractor have a great influence on the results. It is not practical to extract for a long time to reach an ideal point for a certain kind of hard rubber. For example, the author vulcanized hard rubber prepared from the mixture: rubber 100, sulfur 40, tetramethylthiuram monosulfide 2, zinc oxide 10, stearic acid 1, for 30 and 120 minutes at 141° C. Two vulcanized products containing approximately 1 and 10 per cent free sulfur were extracted with the new apparatus. The amounts of extract were determined at various stages of the extraction. The organic acetone extract or "corrected acetone extract" was estimated by substracting the free sulfur (the method of analysis is described later). The results are shown in Table I.

TABLE I

		Acetone Extraction (Hours)								
		5	10	20	30	40	60	80	100	150
Acetone ext., per cent	(a)	1.84	2.77	2.78	2.79	2.94	2.98	3.08	3.77	4.15
Acetone ext., per cent	(b)	3.29	3.33	3.57	3.68	3.72	3.79	3.94	4.12	4.83
Free sulfur, per cent	(a)	9.24	9.35	9.46	9.47	9.47	9.58	9.60	9.66	9.70
Free sulfur, per cent	(b)	0.84	1.02	1.00	1.00	1.00	1.01	1.01	1.11	1.20

(a) is vulcanized for 30 minutes and (b) for 120 minutes.

It is clear from this table that the free sulfur extracted continues to increase slightly even after 150 hours, and there seems to be no end-point. The results of this experiment and those of Stevens,[11] who extracted for 44 to 1210 hours two samples prepared from the mixture: crepe 100, sulfur 75, zinc oxide 20, zinc diethylthiocarbamate 5 (vulcanized at 100° C. for 336 hours) or zinc sulfide 5 (vulcanized at 150° C. for 4.5 hours), in which case the acetone extract increased steadily, indicate that extension of the time of extraction over 150 hours does not give an end-point.

The corrected acetone extract indicates steady increases up to 150 hours; the rates of increase were higher than those of free sulfur. This difference may be explained by differences of solubility; *e. g.*, free sulfur can be extracted more easily than organic acetone-soluble substances. The results of these two experiments show that extraction for so long a time does not reach an end-point, and there may be danger of chemical changes such as depolymerization as the result of long extraction with heating.

The following preliminary tests of several mixtures containing different percentages of accelerator and sulfur were made with a view to establishing a standard time of acetone extraction.

Mixtures of smoked sheet 100, sulfur 5, 25, 50, 100, and 150, zinc oxide 10, stearic acid 1, diphenylguanidine 2, were vulcanized at 141° C. for 60, 180, and 300 minutes.

The method of preparation of the samples and the apparatus used were the same as in the preceding experiments. Tests of the extraction were made every 2 hours of continuous extraction up to 10–20 hours, after which an interval of time of 10 hours was set. The results of 50 hours' extraction are given in Tables II and III.

The results of successive extractions, shown in Table III, indicate that the corrected acetone extract reached 75–85 per cent (81 per cent of total average from the table) of the 50 hours' extraction after 12 hours' extraction, and 85–95 per cent (92.5 per cent of the total average from the table) after 20 hours' extraction.

However, as indicated in Table I, the organic acetone extract did not reach a constant value by extending the time of extraction over 50 hours; it showed an endless continuous increase which was of a rather doubtful nature. Accordingly, it

was necessary to select a standard time of extraction. Extraction of free sulfur, though not having reached an end-point, was almost the same after 20 hours' as after 50 hours' extraction. At the same time, the organic acetone extracts of various samples were similar after 20 hours' extraction (94.2 per cent of the total average).

The object of this experiment was not to determine the absolute but only the relative amounts of extract, and the changes in the extracts of various compounds after vulcanization. The author's 20-hour extraction was selected as the best to fulfill these requirements.

TABLE II

CORRECTED ACETONE EXTRACTS AND FREE SULFUR VALUES IN PERCENTAGES

Sample			Time of Extraction (Hours)								
			10	12	14	16	18	20	30	40	50
(A)	C. A. E.	(c)	3.60	0.14	0.18	0.10	0.10	0.08	0.05	0.05	0.00
(A)	C. A. E.	(d)	2.51	0.24	0.20	0.17	0.16	0.12	0.15	0.17	0.17
(A)	C. A. E.	(e)	2.93	0.21	0.21	0.14	0.11	0.05	0.18	0.14	0.15
(A)	F. S	(c)	0.26	0.08	0.03	0.01	0.00	0.00	0.00	0.00	0.00
(A)	F. S	(d)	0.17	0.04	0.04	0.03	0.02	0.03	0.03	0.02	0.03
(A)	F. S	(e)	0.25	0.04	0.03	0.04	0.04	0.03	0.03	0.03	0.02
(B)	C. A. E.	(c)	2.00	0.06	0.13	0.13	0.10	0.11	0.05	0.06	0.09
(B)	C. A. E.	(d)	3.18	0.06	0.18	0.06	0.05	0.05	0.10	0.12	0.07
(B)	C. A. E.	(e)	2.84	0.14	0.11	0.05	0.09	0.15	0.10	0.07	0.07
(B)	F. S	(c)	7.60	0.05	0.05	0.05	0.04	0.04	0.07	0.06	0.05
(B)	F. S	(d)	0.20	0.03	0.04	0.04	0.03	0.03	0.03	0.03	0.03
(B)	F. S	(e)	0.21	0.04	0.04	0.02	0.02	0.00	0.00	0.02	0.02
(C)	C. A. E.	(c)	2.51	0.11	0.05	0.04	0.07	0.08	0.07	0.07	0.06
(C)	C. A. E.	(d)	2.67	0.19	0.17	0.08	0.05	0.05	0.10	0.06	0.06
(C)	C. A. E.	(e)	2.94	0.08	0.06	0.05	0.07	0.04	0.15	0.08	0.07
(C)	F. S	(c)	20.02	0.05	0.04	0.05	0.06	0.04	0.08	0.05	0.04
(C)	F. S	(d)	3.35	0.04	0.03	0.02	0.00	0.00	0.04	0.04	0.04
(C)	F. S	(e)	1.56	0.07	0.04	0.05	0.00	0.04	0.05	0.07	0.03
(D)	C. A. E.	(c)	2.95	0.17	0.13	0.07	0.10	0.06	0.07	0.05	0.05
(D)	C. A. E.	(d)	2.13	0.10	0.06	0.04	0.04	0.03	0.06	0.07	0.09
(D)	C. A. E.	(e)	1.44	0.20	0.13	0.03	0.05	0.05	0.05	0.09	0.12
(D)	F. S	(c)	33.95	0.03	0.02	0.03	0.02	0.02	0.03	0.03	0.00
(D)	F. S	(d)	15.38	0.10	0.09	0.06	0.04	0.07	0.12	0.08	0.06
(D)	F. S	(e)	13.59	0.17	0.10	0.11	0.07	0.07	0.18	0.13	0.08
(E)	C. A. E.	(c)	2.73	0.20	0.11	0.12	0.12	0.06	0.07	0.07	0.10
(E)	C. A. E.	(d)	2.50	0.08	0.08	0.06	0.10	0.14	0.13	0.15	0.18
(E)	C. A. E.	(e)	1.50	0.12	0.09	0.08	0.06	0.10	0.04	0.02	0.04
(E)	F. S	(c)	44.20	0.02	0.02	0.03	0.03	0.02	0.03	0.03	0.04
(E)	F. S	(d)	27.19	0.15	0.12	0.11	0.06	0.03	0.13	0.10	0.10
(E)	F. S	(e)	23.55	0.36	0.22	0.20	0.14	0.08	0.20	0.18	0.16

Note: The percentages of sulfur used in the compound were: Sample A 5, B 25, C 50, D 100, and E 150; the time of vulcanization of (c) was 60 minutes, (d) 180 minutes, and (e) 300 minutes. C. A. E. designates corrected acetone extract and F. S designates free sulfur.

For estimating the free sulfur necessary for calculating the corrected acetone extract, the British Standard Specification, Appendix No. III, Method (*loc. cit.*) was used, *i. e.*, the acetone extract was heated with fuming nitric acid, with addition of potassium chlorate from time to time to accelerate oxidation; after complete oxidation the mixture was evaporated to dryness by adding concentrated hydrochloric acid and sodium chloride, was acidified with dilute hydrochloric acid, was heated, and the free sulfur was determined by precipitation as barium sulfate in the ordinary way.

TABLE III

Sample			Total Ext. in 12 Hours	Percentage of 50-Hr. Extraction	Total Ext. in 20 Hours	Percentage of 50-Hr. Extraction	Total Ext. in 50 Hours
(A)	C. A. E.	(c)	3.74	87.0	4.20	97.8	4.30
(A)	C. A. E.	(d)	2.75	70.7	3.40	87.5	3.89
(A)	C. A. E.	(e)	3.14	76.3	3.65	88.6	4.12
(A)	F. S	(c)	0.34	89.5	0.38	100.0	0.38
(A)	F. S	(d)	0.21	51.2	0.33	80.5	0.41
(A)	F. S	(e)	0.29	56.9	0.43	84.3	0.51
(B)	C. A. E.	(c)	2.16	76.4	2.63	93.0	2.83
(B)	C. A. E.	(d)	3.34	84.1	3.68	92.7	3.97
(B)	C. A. E.	(e)	2.98	82.4	3.38	93.5	3.62
(B)	F. S	(c)	8.06	95.7	8.24	97.8	8.42
(B)	F. S	(d)	0.23	50.0	0.37	80.5	0.46
(B)	F. S	(e)	0.25	67.6	0.33	89.2	0.37
(C)	C. A. E.	(c)	2.62	85.6	2.86	93.5	3.06
(C)	C. A. E.	(d)	2.86	83.4	3.21	93.7	3.43
(C)	C. A. E.	(e)	3.02	85.4	3.24	91.6	3.54
(C)	F. S	(c)	20.07	98.4	20.26	99.3	20.43
(C)	F. S	(d)	3.39	95.3	3.44	96.7	3.56
(C)	F. S	(e)	1.63	85.4	1.76	92.1	1.91
(D)	C. A. E.	(c)	3.12	85.5	3.48	95.5	3.65
(D)	C. A. E.	(d)	2.23	85.2	2.40	91.6	2.62
(D)	C. A. E.	(e)	1.64	76.0	1.90	88.0	2.16
(D)	F. S	(c)	33.98	99.7	34.07	99.9	34.13
(D)	F. S	(d)	15.38	96.7	15.64	98.4	15.90
(D)	F. S	(e)	13.59	94.8	13.93	97.3	14.33
(E)	C. A. E.	(c)	2.93	81.9	3.34	93.3	3.58
(E)	C. A. E.	(d)	2.58	75.5	2.96	86.6	3.42
(E)	C. A. E.	(e)	1.62	79.0	1.95	95.2	2.05
(E)	F. S	(c)	44.22	99.6	44.32	99.8	44.42
(E)	F. S	(d)	27.34	97.6	27.66	99.0	27.99
(E)	F. S	(e)	23.91	95.3	24.55	97.7	25.09

II. Changes in Acetone Extract

The observed changes in the acetone extract during vulcanization under similar conditions of the same compounds, as described in the first Communication, show that the extract increases for a certain period at the beginning of vulcanization; then there is a general tendency to diminish slightly to 60 minutes of vulcanization. At approximately 90 minutes all curves of the acetone extract, regardless of the percentage of total sulfur, showed intermediate maxima, as in the changes in elongation of samples containing less than 25 per cent sulfur, described in the first Communication. These maxima became clearer and more pronounced with higher proportions of sulfur.

It is generally considered that an increase in the acetone-soluble substances of vulcanized rubber is attributable to aging caused by sunlight, oxygen, heat, etc. Since the phenomenon appeared during vulcanization in the present experiments, in which sunlight and air played no part, it must here be attributed to aging caused by heating, assuming that an increase in acetone extract is caused by the aging of vulcanized rubber.

That vulcanized rubber changes into acetone-soluble substances as a result of aging by heat is clear from the studies of Stevens.[12] However, the changes in the percentage of acetone-soluble substances during vulcanization are not a simple and steady increase or decrease, since the curves of acetone-soluble substances have maxima corresponding to definite times of vulcanization probably due to the effect of temporary depolymerization at the beginning of vulcanization by the action of

accelerators and heat; at the same time, polymerization goes on as a result of heating the vulcanized rubber, and this decreases the acetone-soluble substances. In other words, depolymerization and polymerization progress in opposition to each other, and the formation of acetone-soluble substances is governed by the sum of these two reactions. The net result depends on the content of resinous substances in the raw rubber and the effect of compounding ingredients. The existence of a maximum point in the acetone extract at approximately 90 minutes in all cases is closely related to the characteristic changes in elongation, as described in the first Communication. Accordingly, this corresponds to a point in the formation of hard rubber where the tensile strength and hardness increase rapidly. The acetone extract increases rapidly for a while, as a result of depolymerization of vulcanized rubber, and reaches a maximum point, after which there is a tendency to diminish gradually as the sudden increase in polymerization of hard rubber overbalances the rate of depolymerization. In the case of hard rubber mixtures containing large percentages of sulfur, the acetone-soluble substances probably diminish gradually as self-polymerization becomes greater.

Summary

1. To explain chemically the fundamental hard rubber reactions which take place during the vulcanization, changes in the acetone-extractable substances, as well as in tensile strength, elongation, and hardness, during vulcanization were studied.

2. Preliminary experiments on acetone extraction with the author's apparatus indicated that a 20-hour extraction was ideal for the purposes of the investigation, and extractions extending to extremely long periods were unsuitable in the present experiments.

3. The corrected acetone extract or organic acetone-soluble substances do not either increase or diminish steadily throughout vulcanization, but show a maximum value at a definite period of vulcanization. The appearance of this maximum value, which also corresponds to characteristic changes in tensile strength, elongation, and hardness (cf. the preceding Communication) is a turning point where the hard rubber reaction diminishes rapidly.

4. To explain chemically the appearance of a maximum value and consequent increase and decrease in the percentage of acetone-soluble substances (corrected) it may be considered that the rubber or rubber compounds with different degrees of vulcanization are polymerized at a certain period of vulcanization, depending on the action of heat, accelerators and agencies, and that the amount of acetone-soluble substances is governed by these factors.

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[4] Feuchter, *Kolloidchem. Beih.*, **19**, 47 (1924); **20**, 78 (1925).
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[8] British Standard Specification, No. **234**, 1933.
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[10] Caspari, "India Rubber Laboratory Practice," p. 114.
[11] Stevens and Stevens, *J. Soc. Chem. Ind.*, **48**, 55T (1929).
[12] Stevens, *Ibid.*, **38**, 195T (1919).

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Studies of Hard Rubber Reactions

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IV. Coefficients of Vulcanization

The first work in connection with this subject was published by C. O. Weber (*Kolloid-Z.*, **33,** 65 (1906)). Subsequently, Spence and Young (*Kolloid-Z.*, **11,** 65 (1912)) showed that the maximum amount of sulfur capable of combining with rubber was in the neighborhood of 32 per cent, corresponding to $C_{10}H_{16}S_2$, which requires a vulcanization coefficient of 47.

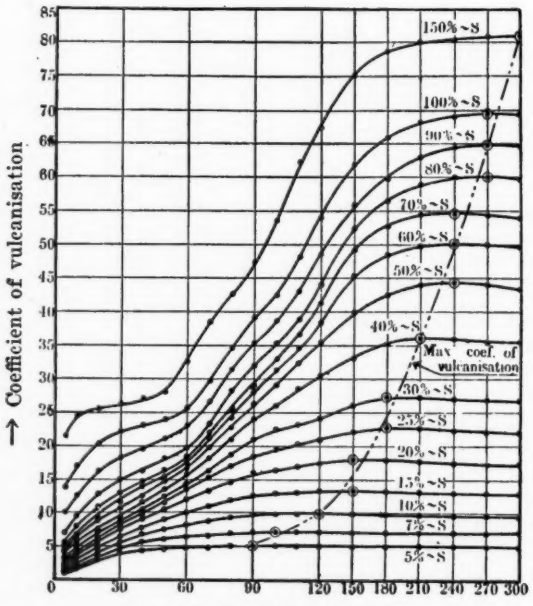

Figure 1

On the other hand, Skellon ("Rubber Industry," London, **1914,** p. 172) indicated that with a sufficient excess of sulfur, vulcanization coefficients exceeding 50 were obtainable, which may be attributed to the production of polysulfides or the formation of insoluble sulfur in hard rubber. In another series of experiments of H. P. Stevens and W. H. Stevens (*J. Soc. Chem. Ind.*, **48,** 55T (1929)), it was shown that by prolonged vulcanization at temperatures as low as 100° C., employing sulfur 2 to 10 times the weight of rubber and zinc diethyldithiocarbamate as an accelerator, the combined sulfur might be increased considerably more than

47 per cent. Fisher and Schubert (*Ind. Eng. Chem.*, **26**, 209 (1936)) have also noted that when the amount of sulfur used is greater than the theoretical ratio, the combined sulfur may be greater than 32.02 per cent, indicating that some of it has replaced hydrogen.

There are, however, still some ambiguous points to be settled by further investigation; whether for example sulfur combines with rubber to such a wide ex-

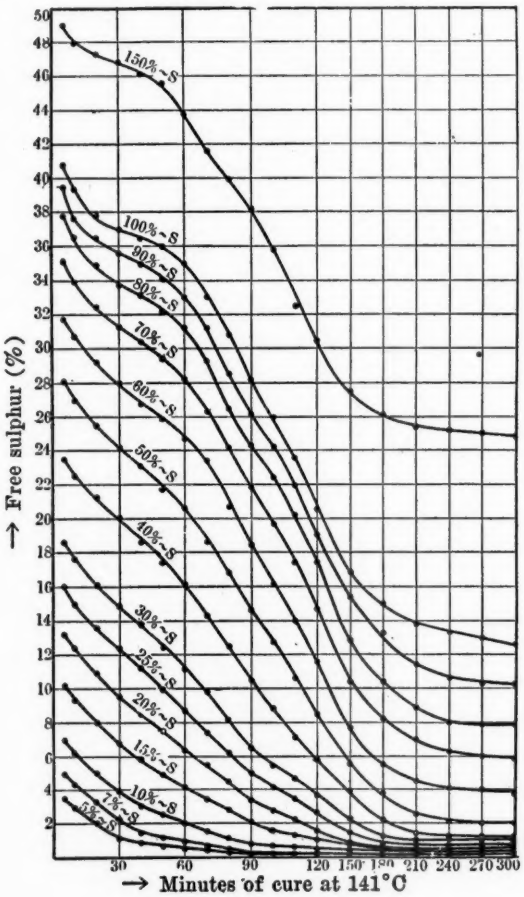

Figure 2

tent regardless of the theoretical or maximum coefficient of vulcanization, especially using organic accelerators.

Experimental

As regards the mastication of rubber, mixing, vulcanizing, etc., and also the composition of the mix, the experimental procedure was similar to that previously reported. (See Part I.)

The total sulfur was determined as prescribed by the Society of Rubber Industry of Japan or the American Method (*Ind. Eng. Chem.*, **16**, 397 (1924)), and the

coefficients of vulcanization were calculated from the difference between the total sulfur and the original free sulfur (estimated as in Part III) based on the pure rubber hydrocarbon content in raw rubber, which was assumed to be 93 per cent.

The above calculation is based on the assumption that the sulfur in the acetone extract exists in ordinary elemental form and no other sulfides are in vulcanized rubber except that of rubber and sulfur. However, the acetone extracts in general may be partly associated with sulfur derivatives of rubber degradation products

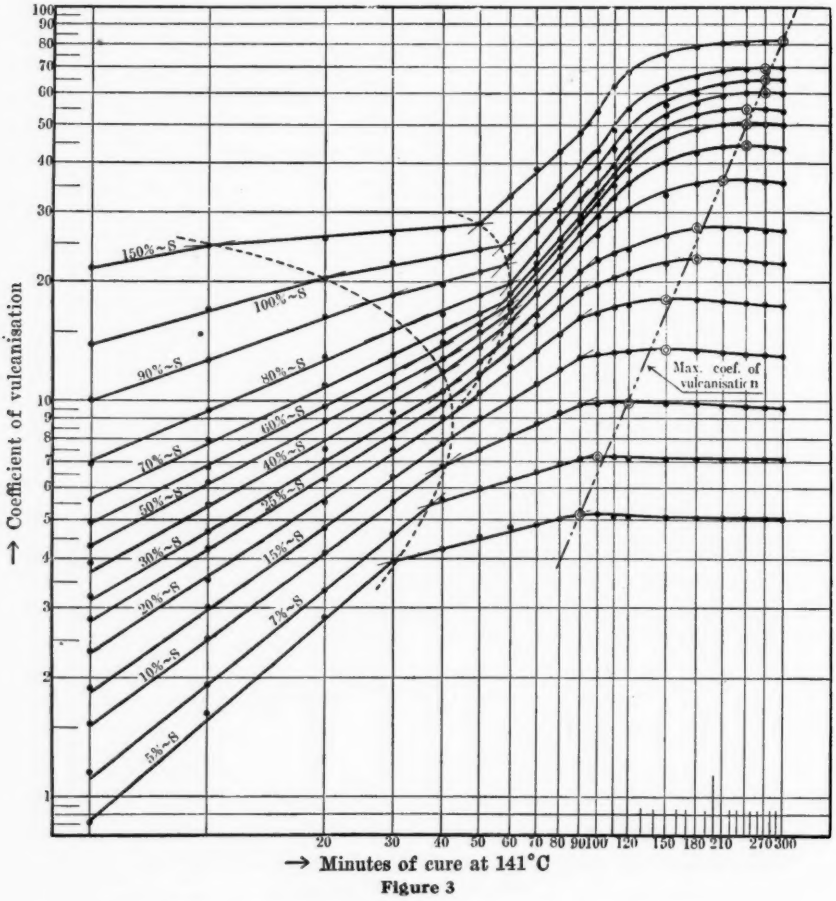

Figure 3

and reaction products of sulfur with resins, proteins, etc., and, furthermore, the vulcanized rubber products, even after extraction with acetone, may contain acetone-insoluble sulfides of resins, proteins, and other metallic sulfides. The corrections for this will be reported later.

Summary of Results

The results of the experiments are plotted in Figs. 1 to 3, and the main characteristics may be illustrated briefly as follows:

(1) With low-sulfur compounds, such as 5 to 15 per cent of sulfur, any marked

changes in the curves were hardly observed, but all compounds containing more than 20 per cent of sulfur showed a small, rapid increase in combined sulfur in the neighborhood of 90 minutes, and then a gradual increase for a short time, indicating that at this stage of cure some of the sulfur once combined might be liberated again.

(2) When the above-mentioned time of about 90 minutes was passed, the coefficients of vulcanization of high sulfur stocks began to increase abruptly and reached a maximum value, but in almost all cases it decreased subsequently in spite of the presence of free sulfur (see Fig. 2).

(3) Up to 60 per cent of sulfur, the coefficients of vulcanization exceeded the theoretical value of 47, and with a very large excess of sulfur, *e. g.*, 150 per cent, it reached values above 80.

Comparing the author's vulcanization curves with those obtained by C. O. Weber and by Spence and Young, some notable facts are obvious. In Weber's curves, as is well known, there are nicks in various parts. Spence and Young concluded that Weber's breaks in the curves are probably due to experimental errors. In the case of the present author's curves, each cure was conducted for an interval of a certain number of minutes, and breaks in the curves were found which closely resembled Weber's curves in some respects. In a similar manner, however, smooth curves like those of Spence and Young were also obtained by adopting cure intervals of 40 minutes.

The author came to the conclusion that the difference between the two types of vulcanization curves might have resulted from the fact that longer cure intervals like those of Spence and Young lead to the elimination of the thermally active part of vulcanization, corresponding to about 90 minutes in the author's experiments, while the essential phenomenon was shown in Weber's curves.

(4) As shown in Fig. 3, the vulcanization curves represented by logarithmic coördinates can be divided into three groups of straight lines or curves.

The first group of lines may be considered to be the primary reaction of soft rubber, or its polymerization. After a certain number of minutes of cure, the linear curves changed discontinuously, showing the occurrence of the secondary reaction of polymerization of semi-hard rubber. In this case, however, specimens containing excess sulfur, *e. g.*, more than 25 per cent, showed intermediately other straight lines attributable to special sulfur compounds. It was observed finally that after 90 minutes the tertiary reaction of characteristic hard rubber vulcanization or polymerization had taken place.

V. Loss of Total Sulfur during Vulcanization

In a previous work (*J. Soc. Chem. Ind., Japan*, **40**, 111B (1937)) it was observed that after the highest coefficient of vulcanization had once been attained, it decreased gradually in all cases, indicating loss of combined sulfur. In this section, experiments are described wherein the losses of the total sulfur in the whole course of hard-rubber vulcanization were determined, and some attempt was made to deduce the relation between the loss of total sulfur and the tensile strength of hard rubber.

Experimental

Mastication of the rubber, mixing, curing, composition of the mix, and experimental procedure were the same as in the previous experiments (in Part I), except that the total sulfur was estimated by means of the method described in Part IV.

Summary of Results

As shown in Fig. 1, all the compounds containing 5 to 150 per cent of sulfur (based on the rubber) indicated a gradual loss of total sulfur, with a relatively

rapid loss after about 90 minutes, which corresponds to the period of the hard rubber reaction.

Some investigators hold the view that the loss of total sulfur is the result of liberation of hydrogen sulfide by the interaction of sulfur with rubber, resins, and proteins, and sublimation of sulfur. In the present experiments, the cause of the comparatively marked loss of total sulfur seems to be related to the hardening or polymerization reaction in hard rubber. No good mixture could be obtained

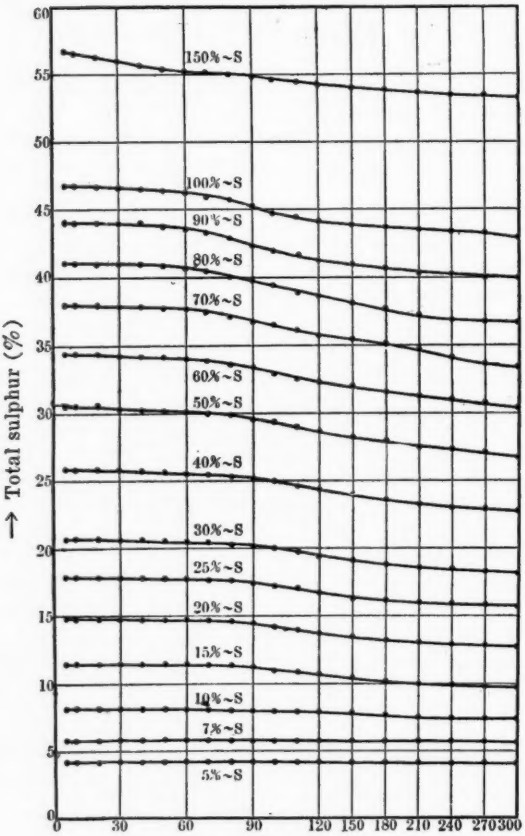

Figure 1

from which the maximum loss of total sulfur was reached, with reference to the content of rubber, *i. e.*, rubber resins, proteins, and that of sulfur. The loss of sulfur by sublimation was restricted as far as possible by enveloping the samples with cellophane.

It appears from these facts that the depolymerization phenomena of soft or semi-hard rubber products may occur during the initial stage of vulcanization and those of the hard rubber after 90 minutes.

Considering again the vulcanization curves in the previous report (Part IV), there is no loss of sulfur in the initial stage of vulcanization but considerable losses

of sulfur are seen in the present curves of total sulfur; in other words, during the whole course of vulcanization the combined sulfur increases to a certain extent, accompanying the loss of sulfur on one side.

In Fig. 2, the relationship between the loss of total sulfur and the tensile strength

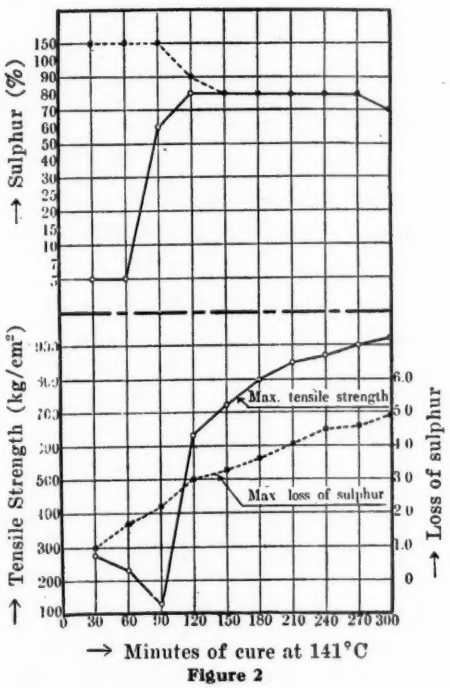

Figure 2

of the hard rubber product is shown. Of all the hard rubber compounds, the samples containing 70–80 per cent of sulfur showed the maximum loss of sulfur, coinciding with the maximum tensile strength after vulcanization for 90 minutes. It may be assumed that the polymerization and the depolymerization reactions occur simultaneously and are closely related.

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Expanded Chlorinated Rubber

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In a previous publication (*J. Soc. Chem. Ind.*, **54**, 263T–267T (1935); RUBBER CHEM. AND TECH., **8**, 613 (1935)) some particulars were given regarding the production and development of a hard spongy material from chlorinated rubber (British Patent No. 424,561).

Thermal and Electrical Properties

Some preliminary tests on the thermal and electrical properties of the material have now been carried out, and these serve to confirm the view that expanded chlorinated rubber should prove to be a very good insulating material.

Thermal Conductivity.—The details given herewith are taken from a report by the Research Association of British Rubber Manufacturers.

The thermal conductivity was determined by comparison with cork, a good insulating material of which the thermal properties are fairly well known. The method used consisted in placing slabs of cellular rubber and of cork each between a pair of aluminum plates, and then interposing between the two sets of plates an electric heating plate made of wire enclosed between sheets of mica. The plates, heater, and sheets of expanded chlorinated rubber material and cork were all of the same size, namely, 20.3 by 10.25 cm. The aluminum plates were 0.625 cm. thick.

Each aluminum plate had three iron-constantan wire thermocouples in it, by which its mean temperature could be measured. The whole was placed in a thermostatically controlled oven kept at 22.5 ± 0.5° C., the wires from the heater and thermocouples being taken to the measuring instruments through a small hole. In this way the temperatures of the plates could be measured without opening the oven door and so causing cold air to enter and upset the equilibrium.

In carrying out the test the heating current (0.488 amp., 11.22 volts) was switched on and the whole left until equilibrium was attained, as indicated by the temperatures of the four plates becoming steady. The thicknesses of the slabs of cork and cellular rubber were so adjusted that the two outside aluminum plates were at practically the same temperature, which means that the temperatures of the inside plates also must be practically equal. Under these conditions the amounts of heat conducted through the cork and cellular rubber are substantially equal, so that their thermal conductivities must be approximately proportional to their respective thicknesses.

It was found that with cellular rubber 1.4 cm. thick and cork 2.3 cm. thick, the temperatures of the aluminum plates approximately satisfied the conditions just stated, being (in the order shown above): 25.3°, 43.4°, 43.9°, and 24.7° C. The temperature of the surrounding air was 22.7° C. Taking the thermal conductivity of cork as 0.000097 (as given in the literature for cork of the specific gravity used) the conductivity of the cellular rubber is thus about 0.000097 by 1.4/2.3, *i. e.*, 0.000059.

This method of calculation is only approximate because the outside plates cannot be brought to exactly the same temperature, and a small additional error arises from the difference in heat radiated from the edges of the cork and cellular rubber, owing to their differing thickness. It is possible to allow for these disturbing fac-

tors by a more elaborate method of calculation which need not be detailed here. This gives the conductivity of cellular rubber as 0.000048.

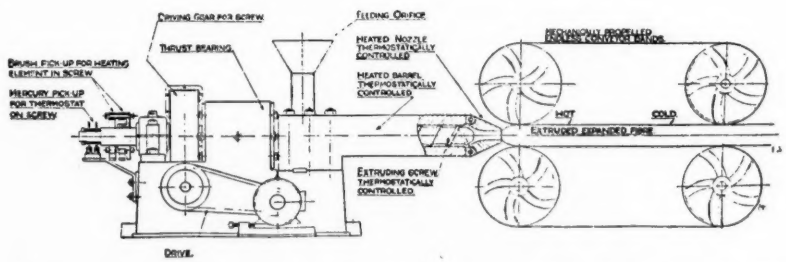
In view of the difficulty of measuring the heat conductivity of such a good insulating material, and the fact that the samples of cellular rubber were far from uniform in texture, no great accuracy can be claimed for these results. It may be concluded, however, that the conductivity of the samples was of the order of 0.00005 cal. per sec. for a 1 cm. cube with 1° C. temperature difference between opposite faces. The sample of cellular chlorinated rubber thus shows a marked advantage over cork, which is generally considered to be an excellent heat insulator.

Electrical Properties. (*a*) *Surface Resistivity.*—Thin strips 50 by 10 by 1 mm. were cut from the samples, and Aquadag (colloidal graphite) electrodes were painted down each long edge so as to leave a strip 50 by 5 mm. uncovered down the center of each side. These samples were supported in glass tubes by wires attached to the electrodes and kept at 75 per cent R. H. by means of saturated sodium chloride solution. The samples were conditioned thus in the dark for 48 hours before testing.

The resistivity was measured by determining the rate of leak when 500 volts were

EXPANDED CHLORINATED RUBBER.

SPECIAL EXTRUDING MACHINE



applied across the electrodes. This leak was measured by means of a Lindemann electrometer with a 0.01 mfd. condenser in parallel to reduce the sensitivity.

The surface resistivity was found to be 1.6×10^{13} ohms per sq. cm.

British Standards Specification No. 488/1933 requires a surface resistivity of 10^{11} ohms per sq. cm. Inasmuch as the figures for E. C. R. are considerably higher, it is obvious that the surface resistivity is of a high order. As a further comparison in regard to surface resistivity, it may be mentioned that the surface resistivity of a specimen of an average phenol-formaldehyde plastic was found to be 3×10^{11} ohms per sq. cm.

(*b*) *Volume Resistivity.*—With regard to volume resistivity, the values were found to be so high that it was not practicable to obtain satisfactory measurements with the specimens available at the time of testing. It was estimated, however, that the surface resistivity is at least 5×10^{11} ohms per cm. cube.

Commercial Development

Extrusion Machine.—In the paper to which reference is made before, an indication was given of what had been done and what was contemplated from the point of view of manufacturing the material on a commercial scale. Since the paper in question was written, a good deal of development work has been carried out with a view to the production of the material in board form. The illustration on

page 799 shows diagrammatically the method of operation (British Patent Appln. No. 33147/36). It will be observed that the barrel, the extruding screw, and the nozzle of the extruding cylinder are all thermostatically controlled, the heating in this particular form of apparatus being electrical.

Some preliminary experiments have also been carried out with standard types of extrusion machines, such as are used for extruding endless lengths of solid synthetic resins, etc.

It is hoped at a later date to give full working details of methods and processes.

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Extrusion Qualities of Rubber

Effect of Temperature and Mill Roll Opening

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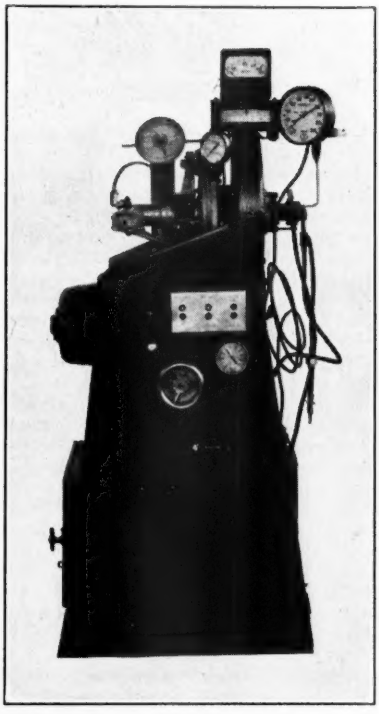
EVERYDAY milling practice shows that rubber becomes softer when milled on a cold mill than when milled for the same length of time on a hot mill, and also that a tight mill will produce softer rubber than an open mill, using the same number of passes. Although this may seem obvious to one who is experienced in rubber milling, the published work on variations in the softness of rubber resulting from differences in roll temperatures and mill roll setting is meager; additional data on this subject would not be unwelcome in rubber literature. Also, a series of tests to determine the effects of these factors on the working qualities of rubber provides a satisfactory means for describing a method for operating a tubing machine plastometer which has proved to be of considerable value in this laboratory.



TUBING MACHINE

Tubing Machine

In this method a small tubing machine was specially built for the purpose:

The temperature is regulated by means of water passing through both barrel and worm at 180° F. (82.2° C.) in a closed system with thermostatic control, and temperature variations of this circulating water are indicated on a dial thermometer plainly visible to the operator. Speed is held constant at 35 r. p. m. of the worm, which is 1.25 inches (3.2 cm.) in diameter with progressively decreasing pitch; the power consumed is indicated on a wattmeter, also in front of the operator. A $^3/_{32}$-inch (2.38-mm.) orifice is used for the extrusion, and built into the head is a thermocouple around which the rubber must pass before extruding. This is connected to a temperature indicator, also in position over the machine. The barrel of the tubing machine is free to move back and forth a short distance (0.75 inch, or 19 mm.) and is rigidly attached to a diaphragm operated by air pressure. This air pressure, obtained from a small tank under the machine, is maintained constant at 20 pounds per square inch (1.406 kg. per sq. cm.) and, when applied to the diaphragm, pulls the barrel back with a force of 1380 pounds (625.97 kg.). The motion of the barrel is indicated on a dial placed behind the machine, also in view of the operator.

Plasticity Determinations

In the operation of this tubing machine for determining the plasticity of a sample, the rubber is cut into pieces small enough to be easily fed into the hopper. The cold rubber is fed at a uniform rate with the air pressure off, so that the barrel is in the forward position with relation to the worm. Exactly 200 grams of the rubber are run through before any readings are taken, in order to bring the rubber in the machine and the die to a constant temperature. Then the tubing is continued with additional rubber, and three one-minute samples are cut off by means of the cutter fastened in front of the die. During the extrusion of these three samples, temperature of the extruding rubber is recorded and average power readings are taken. Any variations in the circulating water temperature are also noted. The three samples are weighed individually, and the average is taken and recorded as "grams extruded per minute," which for brevity is called G_x. The worm is then stopped with the machine loaded and held for exactly 3 minutes. Then the air valve is opened, and the 20 pounds per square inch pressure is applied to the diaphragm which forces the die back against the rubber in the space between the die and screw with a pressure of 1380 pounds. The movement of the barrel backward as the rubber is forced out of the die is indicated on the dial back of the machine, and the divisions on the dial correspond to the volume of rubber extruded. With a stop watch the number of minutes to extrude 5.4 cc. are taken and recorded as M. This completes the test, and the machine is cleaned out; each test is started with an empty machine.

The factor G_x is a direct measure of tubeability or tubing speed, and M is an inverse measure of plastic flow. G_x/M, for want of a better word, is called "plasticity."

Figure 1 and the following table give results on four 400-gram samples taken from the same slab of factory milled and blended smoked sheet which were ground for 4, 6, 8, and 10 minutes on a 12 × 6 inch (30.48 × 15.24 cm.) laboratory mill, front roll speed 22 r. p. m., back roll speed 32 r. p. m., ratio 1.45 to 1, roll temperature maintained at average of 90° F. (32.2° C.), and opening between rolls 0.010 inch (2.54 mm.):

Grinding Time *Min.*	G_x	M	G_x/M
4	37.02	0.4	92.6
6	47.07	0.2	235.4
8	52.81	0.11	480.5
10	57.21	0.08	715.0

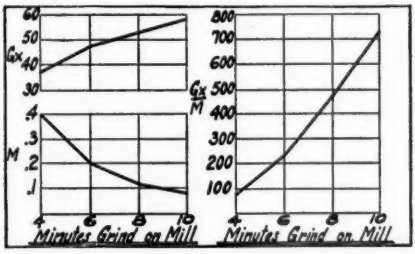


FIGURE 1. RESULTS OF EXTRUSION TESTS

These figures serve to illustrate the magnitude of differences in plasticity readings, even when samples are taken with only 2-minute variations in grinding.

Effect of Temperature and Roll Setting

In order to determine the effect on the rubber tubing qualities and plastic flow of the variations in roll temperature and roll settings, fifteen 400-gram samples, taken from a slab of factory milled and blended smoked sheet, were treated on the same laboratory mill as follows: Each passed through the rolls exactly ten times. Five samples were subjected to a roll temperature of 90° F. (32.2° C.) and openings between

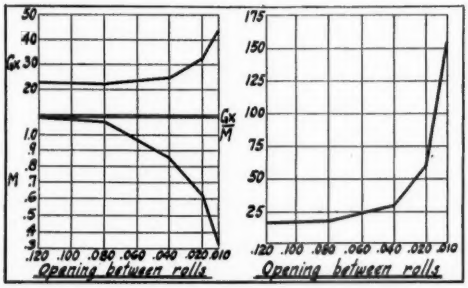


FIGURE 2. EFFECT OF SIZE OF MILL OPENING ON EXTRUSION QUALITIES

the rolls of 0.010, 0.020, 0.040, 0.080, and 0.120 inch (0.25, 0.51, 1.02, 2.03, and 3.05 mm.), respectively; five to a roll temperature of 165° F. (73.9° C.) and the same openings; and five to a roll temperature of 210° F. (98.9° C.) and the same openings. Samples were tested approximately 24 hours after milling.

The time for making the ten passes decreased as the mill opening increased. Also, the time increased as the roll temperature increased, as the spring of the rolls brought them closer together when the rubber on the mill was hot and soft. Table I gives data on samples milled at the three temperatures.

Figure 2 shows the effect of variations in mill openings, in each case the average of the three temperatures; Figure 3

TABLE I. EFFECT OF TEMPERATURE AND ROLL SETTING ON RUBBER PROPERTIES

Mill Opening *Mm.*	Mill Temp. at End ° *C.*	Time of Ten Passes *Min.*	G_x	M	G_x/M Original	G_x/M Increase from original[a]	G_x/M % increase from original
			Mill Temp. at Start, 32.2° C.				
0.25	46.1	6	45.97	0.20	230	213.5	1293
0.51	40.6	3	35.90	0.44	81.5	65.0	393
1.02	37.2	2	28.21	0.75	37.6	21.1	128
2.03	33.3	1	24.34	1.04	23.4	6.9	42
3.05	32.2	0.9	23.89	1.03	23.2	6.7	41
			Mill Temp. at Start, 73.9° C				
0.25	81.1	7.7	44.71	0.27	165.5	149.0	903
0.51	79.4	3.8	32.22	0.56	57.5	41.0	248
1.02	76.7	2.1	25.77	0.86	29.9	13.4	81
2.03	73.9	1.2	24.07	1.09	22.1	5.6	33
3.05	73.9	1.0	23.39	1.13	20.7	4.2	25
			Mill Temp. at Start, 98.9° C.				
0.25	98.9	11.5	35.67	0.45	79.3	62.8	381
0.51	98.9	5.7	24.93	0.83	30.1	13.6	82
1.02	98.9	2.3	23.76	0.97	24.5	8.0	48
2.03	98.9	1.3	22.44	1.14	19.7	3.2	19
3.05	98.9	1.1	23.93	1.30	18.4	1.9	12

[a] G_x/M on original factory slab, 16.5.

shows the effect of temperature, in each case the average of the five mill openings.

Another test was run to determine the effect of temperature by using the tubing machine as a plasticizer and running samples of the same smoked sheet through the machine once each with the circulating water temperature varying

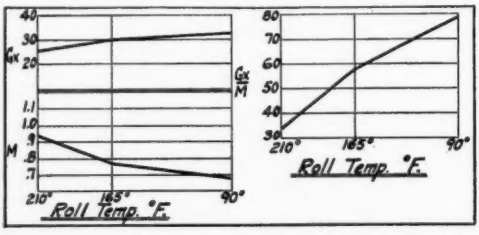


FIGURE 3. EFFECT OF TEMPERATURE ON EXTRUSION QUALITIES

between 120° F. (48.9° C.) and 200° F. (93.3° C.). After passing 400 grams of the rubber through the machine, it was run through the laboratory mill twice with the 3.05-mm. opening and a temperature of 210° F. (98.9° C.) to sheet it out; it was then held approximately 24 hours before testing for plasticity. The following table gives the data obtained in running the rubber through the machine at the various temperatures:

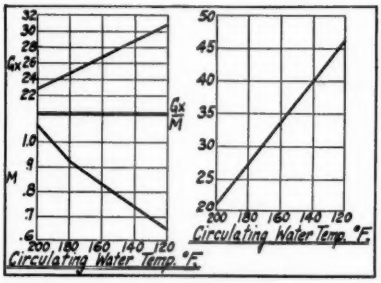


FIGURE 4. EFFECT OF WATER TEMPERATURE ON EXTRUSION QUALITIES

Sample No.	Circulating Water Temp. ° C.	Temp. of Extruding Rubber ° C.	Temp. Rise ° C.	Av. Watts
1	48.9	73.9	25	450
2	60.0	83.9	23.9	350
3	71.1	88.3	17.2	250
4	82.2	94.4	12.2	170
5	93.3	103.9	10.6	140

As is to be expected, the lower the temperature of the barrel and worm, the greater the temperature rise between the water temperature and that of the rubber extruding through the die, and the greater the power consumption.

Figure 4 and the following table show the effect on the extrusion qualities of the variation in circulating water temperature:

Sample No.	G_x	M	G_x/M Original	G_x/M Increase from original[a]	G_x/M % increase from original
1	30.42	0.65	46.8	30.3	183
2	29.02	0.77	37.7	21.2	128
3	27.05	0.84	32.2	15.9	96
4	25.50	0.91	28.0	11.5	70
5	22.41	1.07	20.9	4.4	27

[a] G_x/M on original rubber, 16.5.

Relation of Tubeability and Plastic Flow

All of the data presented thus far show a direct relation between tubeability and plastic flow, and conclusions would be identical if either G_x or M were used and G_x/M omitted. However, G_x and M have a direct relation when the same

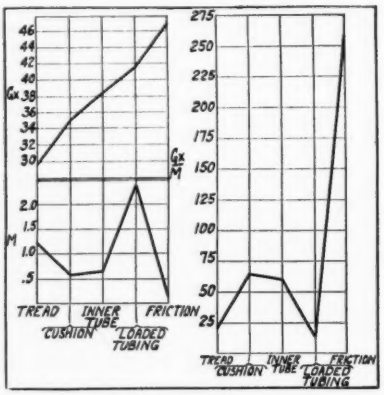


FIGURE 5. RELATION OF TUBEABILITY AND PLASTIC FLOW

type of rubber or compound is compared, but not always when different types of rubber or different compounds are compared. For example, if we draw a curve of the G_x values of five different types of rubber compounds and then below this show the M values, it becomes evident that tubeability and plastic flow are not directly related. Although the G_x/M figure may mean little mathematically, it is a good index of the actual softness of the stock; if stocks are graded arbitrarily by "feel" on the mill, they fall into line with the G_x/M figure more closely than with either G_x or M. These data are given in Figure 5 and the following table:

	G_x*	M	G_x/M
Tread compound	29.7	1.23	24.2
Cushion	35.2	0.51	68.6
Inner tube	38.2	0.58	65.8
Loaded tubing	41.5	2.44	17.0
Friction	46.9	0.18	260.5

* Corrected to 0.92 specific gravity.

In this paper only one procedure for the successful operation of this tubed machine plastometer has been described. A discussion of other procedures designed for factory control of stocks which permit of rapid testing of samples, for development of stocks of certain desired characteristics, for determination of tubing and plastic properties of pigments, for scorch tests of compounds would provide data enough for a number of papers.

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Impact Resilience in Testing Channel Black

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THE precise grading of carbon black has been a problem to rubber manufacturers for years. Empirical specification tests inherited from the paint and ink industries have been used extensively; although they may have great merit in predicting the behavior of a black in paint or ink, they generally tell very little of its value in rubber. Since neither these tests nor the usual stress-strain data showed any great differences that could be associated with type of carbon black, chemists have been inclined to believe in the past that the rubber grade of channel black was quite a uniform material, at least when used in mercaptobenzothiazole stocks.

Among the tests which have been used recently in the grading of black is resilience of the cured stock as determined by an impact pendulum. Although superficially it seems to measure no fundamental property of the black, it is a very practical test from a laboratory standpoint and appears to be capable of at least rough correlation with more fundamental properties. It is not a new property; the fact that it is influenced by carbon black is not new; but its application to the separation of blacks within the range of rubber channel black is new, and this phase will be discussed here.

History

As the term implies, impact resilience involves rapid deformation and forces which are largely compressive. More specifically, it is a measure of the amount of energy which can be returned by the rubber after a rapid blow. There have been several publications on the subject.

Memmler (*13*) described several falling-ball methods and a pendulum hammer for determining resilience, all of which date back to before 1920.

Healy (*9*) referred to a pendulum impact tester that is capable of measuring both the resilience and the penetration under impact. He reported maximum resilience in the neighborhood of 212° F. (100° C.) and its increase after repeated impacts. He illustrated the deadness and hardness brought about by carbon black.

Goodwin and Park (*8*) applied the present pendulum to the evaluation of carbon black over a broad range extending all the way from the soft blacks to the high-color blacks. They made no mention of significant differences within the range of rubber channel black.

Finally Lüpke (*12*) described an impact resiliometer consisting of a horizontal rod supported on four wires (or cords) to form a geometric pendulum which measures resilience but not indentation.

Apparatus, Corrections, and Calculations

The machine used in this work was designed and built some years ago by George Albertoni under the direction of W. W. Vogt. Although not a copy of Healy's pendulum, it was built subsequent to his and some of its constants are the same (*1*).

Briefly, it consists of a pendulum capable of storing energy, which is equipped with a hammer head for striking the sample, and whose angular rebound after the blow can be measured. The angular reading must be corrected for energy losses in the machine. The penetration of the hammer head into the sample can also be measured. This must be corrected for "permanent set" so that the value of deflection finally reported represents the penetration during the last blow.

Considering that when the pendulum is at rest it contains a certain amount of potential energy which depends solely upon the angle made with the vertical, α, and defining per cent rebound (RB) as the percentage of striking energy that is returned to the sample, it can easily be shown that:

$$\%\,RB = \frac{1 - \cos \alpha}{1 - \cos \alpha_0} \times 100$$

Sample Calculation 1.

Angle of start	15.00°
Corrected angle of rebound, α	12.05°

$$\%\,RB = \frac{1 - \cos 12.05^\circ}{1 - \cos 15.00^\circ} \times 100 = \frac{0.02209}{0.03407} \times 100 = 64.8\%$$

Deflection reading	0.261
Permanent set	0.006
Corrected deflection of last blow	0.255

In practice all of this is performed by means of convenient tables.

Another method of using the pendulum is worthy of mention because it eliminates pawl friction and also magnifies small differences. Probably, however, it also magnifies errors due to such things as faulty mounting of the sample and lateral vibration of the pendulum. The pawls are tied back, and after a half-dozen blows the pendulum is released from 15° and allowed to bounce repeatedly until a reading is obtained between some two definite limits—for example, 4° and 5°. The pendulum is moving very slowly at this point, and the maximum value is not difficult to read.

Following the same line of reasoning as before, let the overall fractional rebound (FR) be:

$$FR = \frac{1 - \cos \alpha}{1 - \cos 15^\circ} \text{ for } n \text{ impacts}$$

Within limits the per cent rebound is nearly independent of the angle of start. Considering it to be entirely independ-

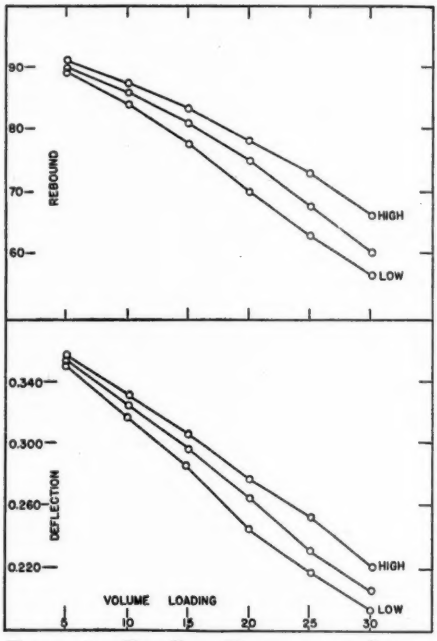

FIGURE 1. PER CENT REBOUND AND INCHES OF DEFLECTION *vs.* BLACK LOADING IN VOLUMES PER 100 VOLUMES OF RUBBER
Three types of black were used.

ent, the over-all fractional rebound for n bounces is given by:

$$FR = \left(\frac{\%\,RB}{100}\right)^n$$

Hence, by this method the per cent rebound is found by taking the nth root of the over-all fractional rebound and multiplying by 100. Since the relation is not rigorously exact, it is advisable always to take the final reading between the same narrow limits (e. g., between 4° and 5°).

SAMPLE CALCULATION 2.

Angle of start	15.00°
No. of impacts	6
Angle of last rebound, α	4.1°

Over-all fractional rebound, $FR = \dfrac{1 - \cos 4.1°}{1 - \cos 15°} = \dfrac{0.00256}{0.03407} = 0.0744$

$\%\,RB = 100\sqrt[6]{0.0744} = 64.9\%$

Deflection same as calculation 1

This calculation also is performed easily by the use of tables.

Variables Affecting Test

Like most other physical tests which are applied to rubber, rebound is influenced by a great many factors such as type

and history of raw materials, and conditions of curing and testing. Various experimental errors, some accidental and some systematic, may creep in at any point between the weighing of the batch and the final recording of the result. A few of these variables will be discussed.

Figure 1 shows three curves of per cent rebound *vs.* black loading. All three curves tend to intercept the zero loading axis at 92 to 93 per cent rebound, which is the value usually obtained with a pure gum stock. They proceed downward to the right, spreading apart at the higher loadings. Hence, for accurate separation of blacks it is advisable to use loadings of at least twenty-five volumes. Although the spread between the extreme blacks may not at first seem very large, it is easily seen from the curves that if twenty-five volumes of the high-rebound black will produce a certain deadness, that same deadness can be produced with only eighteen volumes of the low-rebound black.

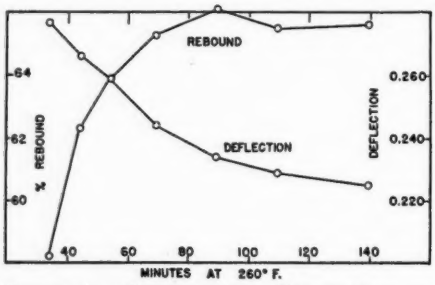

FIGURE 2. REBOUND AND DEFLECTION *vs.* TIME OF CURE (DATA OF TABLE I)

Rebound is comparatively insensitive to state of cure (Figure 2) after the condition of undercure has been passed. But this is not true of deflection. Insensitivity to state of cure is a distinct advantage because it means that no error is introduced when comparing fast- and slow-curing carbon blacks.

On the other hand, rebound is quite sensitive to the temperature of testing (Figure 3). For that reason it has been found essential to condition samples in a constant-temperature bath for some time before testing.

As a sample is struck repeatedly, it becomes more resilient. The biggest change is between

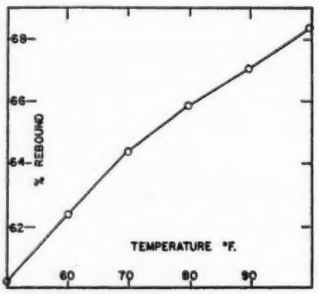

FIGURE 3. REBOUND *vs.* TEMPERATURE

the first and second blows, and after five or six blows it levels off to a fairly constant value. This is not due to the heating of the sample as might be supposed at first but rather is analogous to the change from the first to the *n*th hysteresis loop of a stress-strain curve. In order to eliminate this as a source of error, the practice has been to strike the block until the reading becomes constant.

After precautions have been taken either to eliminate these sources of error or to keep them constant, there is still an irregular day-to-day variation. It is of such magnitude that it is impractical to use the absolute value of per cent rebound as a means of factory control. In this respect the rebound pendulum is not unique, for many other rubber tests have met with the same difficulty. On the other hand, samples of black which have passed through the laboratory as a group should all be subject to the same systematic errors, which would not affect the test when viewed in a relative sense. For want of a better method, we have dealt in terms of "per cent standard;" that is, assigning a value of 100 to the standard, ratings are found for the other samples by direct proportion. This eliminates the systematic error but has the disadvantage that any chance error in the standard is automatically transferred to the relative ratings of all the other samples.

As an example of the errors of testing, the figures of the tables were subjected to a rough analysis. In Table I each figure represents an individual test, and an analysis of this table illustrates the duplicability of tests of the same mixing. In Tables II and III each figure represents an average of several tests. An analysis of these data, therefore, illustrates the exactness with which the absolute value of rebound can be duplicated from mixing to mixing when sufficient tests are run to give a good average. Finally, the same data are given in Table IV on a relative basis; they illustrate how exactly two blacks can be compared from time to time.

Comparison Made	Av. Deviation from Mean
	%
Duplicate tests on same mixing	±0.6
Duplicate mixings of same black (av. 2 to 4 tests):	
Absolute value	±1.1
Relative value	±0.6

It is obvious that complete reliance should not be placed in a test on a single block, and that the relative value is more reliable than the absolute.

Recommended Procedure for Black Testing

Giving due consideration to the variables discussed, the following procedure has been worked out as good practice:

In order to obtain differences between blacks which are of sufficient size to measure accurately, the test formula has been:

Rubber	100	Mercaptobenzothiazole	1
Black	50	Stearic acid	4
Zinc oxide	5	Pine tar	5
Sulfur	3	Phenyl-β-naphthylamine	1
			169

A known black which may be considered a standard of reference is always included with the blacks to be tested and is subjected to exactly the same conditions. For the sake of both efficiency and accuracy the number of unknown samples is usually held between three and seven.

TABLE I. EFFECT OF TIME OF CURE[a]

Min. at 260° F. (126.7° C.)	35	45	55	70	90	100	140
% rebound	57.5	62.5	63.6	65.7	65.2	64.2	65.7
	58.5	62.0	64.2	65.2	66.7	65.7	65.7
	58.5	62.0	63.6	65.7	66.2	66.2	65.2
	58.0	62.0	64.7	65.2	66.2	65.2	65.7
	59.0	62.0	63.6	64.7	66.2	66.2	65.2
	58.5	63.1	63.6	65.2	66.2	65.7	66.2
Av.	58.2	62.3	63.9	65.3	66.1	65.5	65.6
Deflection	0.275	0.267	0.255	0.244	0.233	0.226	0.225
	0.277	0.264	0.261	0.238	0.234	0.230	0.224
	0.276	0.266	0.262	0.246	0.237	0.230	0.224
	0.280	0.264	0.257	0.244	0.233	0.227	0.223
	0.276	0.264	0.258	0.244	0.232	0.232	0.227
	0.278	0.268	0.258	0.245	0.237	0.231	0.226
Av.	0.277	0.266	0.259	0.244	0.234	0.229	0.225

[a] Each figure represents a test on one block. All blocks were from the same batch of stock and were cured on the same day. An average black was used in the test formula. The data are plotted in Figure 2.

Customary good laboratory practice is followed in the selection of rubber and other materials, in milling, in curing, and in resting between the various steps. At least two test blocks are given the same cure, and usually this is done at two points on the flat part of the curing curve (Figure 2)—for example, at 85 and 140 minutes at 260° F. (126.7° C.).

Just prior to test, the blocks are conditioned for 2 hours in water at 82° F. (27.8° C.). They are removed singly from the water, dried, and mounted in the test piece holder. This must be done carefully to avoid distortion. The pendulum is released at least six times from an angle of 15°, and then released repeatedly until the angle of rebound no longer increases. The most frequent value is taken as the angular reading. The deflection reading is taken for several impacts, and finally permanent set is determined. The results in their final form of per cent rebound and deflection are read from tables embodying the corrections and calculations already outlined.

Application of Rebound to Factory Control

Rebound was applied first to the routine testing of carbon black, not because it was thought to measure a desirable

property of a black but because it measured a property that was characteristic of a source. In fact, it was used at first merely as an additional test to obtain as complete data as possible on daily shipments of black. Its interpretation was not hampered by any preconceived ideas. It was considered a new test which was being applied to a virtually unknown material. It appeared statistically, however, that certain sources were producing different types of black from others. Figure 4 shows a few distribution curves, each one representing a source. Source *Y* is of particular interest since its curve has two humps, one forming a definite peak at about 98 and one at about 89. This clearly indicates two producing units so far apart in type of product that their distribution curves are almost entirely separated. Curve *Z* is a recent curve

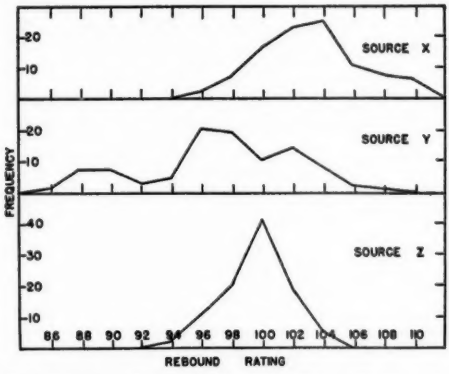

FIGURE 4. FREQUENCY IN PER CENT OF SAMPLES FALLING WITHIN A 2 PER CENT RANGE OF REBOUND RATING, PLOTTED AT THE MIDPOINT OF THAT RANGE

taken on a typical source. It has a higher peak than the others and is spread between narrower limits. There is no question but that it represents a far greater degree of uniformity than the others.

The interpretation of the test came after its use as a routine test. Because of its practical nature it was comparatively easy to use it in selecting type blacks which were then subjected to other tests such as those described below.

Meaning of Rebound as Applied to Black

For years certain blacks—for example, Thermax—have been classed as soft blacks, and various investigators have reported that such soft blacks are of large particle size, gray, relatively nonadsorptive, and capable of incorporation to very high loadings, and that they produce soft uncured stocks and resilient cured stocks, etc. (*6, 7, 8, 11, 14*).

Many papers have been based upon the idea of comparing soft blacks at one extreme with color blacks such as Super Spectra at the other, and have shown differences by a variety of tests. It is of interest, therefore, since a separation has now been made within the normal range of rubber channel black through the use of rebound, to find how many of these other properties vary in the same way as they do over the broader range of all blacks. The most instructive data are found in Table IV in the form of ratings in which black A has been assigned an arbitrary value of 100.

Plasticity of the uncured tread stock as measured by the Williams plastometer is definitely influenced by type of black. Although the correlation of rebound with some properties is

TABLE II. REPEAT TESTS ON SAME SERIES OF BLACKS

	Black A	Black B	Black C	Black D	Black E	Black F	No. of Tests
				Set I[a]			
% rebound:							
85 min. at 260° F.	65.2	61.8	67.3	69.9	65.7	68.5	2
140 min. at 260° F.	65.0	61.5	67.1	69.6	65.7	68.8	2
Deflection:							
85 min. at 260° F.	0.238	0.230	0.244	0.254	0.239	0.253	2
140 min. at 260° F.	0.227	0.218	0.232	0.235	0.231	0.235	2
Nigrometer reading:[b]							
Red	82.4	81.8	82.1	86.3	83.3	84.8	2
Green	85.3	84.6	85.0	89.0	86.0	87.7	2
% net volatile	6.8	4.7	5.9	5.4	4.8	6.4	2
% DPG adsorption[c]	50.8	42.5	38.4	24.9	31.1	53.0	2
				Set II			
% rebound:							
85 min. at 260° F.	66.6	...	...	70.8	66.9	70.0	4
140 min. at 260° F.	66.3	...	...	70.6	66.5	70.7	4
Deflection:							
85 min. at 260° F.	0.246	...	...	0.251	0.242	0.256	4
140 min. at 260° F.	0.229	...	...	0.237	0.228	0.242	4
Nigrometer reading:							
Red	82.1	...	...	85.8	82.8	83.9	2
Green	85.2	...	...	88.8	85.8	87.0	2
% net volatile	5.4	...	...	4.6	4.0	6.4	2
% DPG adsorption	54.4	...	...	25.4	33.4	53.4	2
				Set III			
% rebound:							
85 min. at 260° F.	65.5	...	65.7	68.0	...	68.2	2
140 min. at 260° F.	64.5	...	65.0	69.9	...	69.9	2
Deflection:							
85 min. at 260° F.	0.245	...	0.244	0.253	...	0.254	2
140 min. at 260° F.	0.226	...	0.230	0.241	...	0.239	2
Nigrometer reading:							
Red	81.8	...	83.9	86.7	...	84.5	2
Green	84.8	...	86.8	90.3	...	87.5	2
% net volatile	6.8	...	6.0	4.8	...	6.6	2
% DPG adsorption	53.4	...	36.5	25.3	...	48.8	2
				Set IV			
% rebound:							
85 min. at 260° F.	65.8	63.7	66.6	68.9	...	...	4
140 min. at 260° F.	65.2	63.7	66.3	69.6	...	...	4
Deflection:							
85 min. at 260° F.	0.234	0.230	0.242	0.249	...	...	4
140 min. at 260° F.	0.224	0.215	0.226	0.233	...	...	4
K_1[d]	462	458	412	407	...	...	9

[a] Each set of data is entirely comparable within itself; that is, the processing of the stocks and the running of the tests were so carried out that the relative comparison of each black with black A is reliable.

[b] Nigrometer readings according to Johnson (*11*), using red and green filters.

[c] DPG (diphenylguanidine) adsorption according to Amon and Estelow (*2*).

[d] K_1 determined on a Williams plastometer.

TABLE II. (*Continued*)

	Black A	Black B	Black C	Blank D	Black E	Black F	No. of Tests
				Set V			
% rebound:							
85 min. at 260° F.	66.5	63.2	68.7	70.2	...	...	4
140 min. at 260° F.	65.1	63.1	67.1	69.6	...	...	4
Deflection:							
85 min. at 260° F.	0.236	0.228	0.239	0.245	...	...	4
140 min. at 260° F.	0.223	0.220	0.227	0.233	...	...	4
K_3	470	490	457	415	...	...	12
Nigrometer reading:							
Red	82.8	80.5	83.4	85.0	...	...	1
Green	84.0	82.5	85.8	88.0	...	...	1
% net volatile	6.1	7.1	6.2	4.9	...	...	1
% DPG adsorption	57.1	52.6	42.9	29.1	...	...	1
				Set VI			
% rebound:							
85 min. at 260° F.	67.3	63.5	68.1	71.0	...	...	4
140 min. at 260° F.	66.1	64.7	67.6	71.0	...	...	4
Deflection:							
85 min. at 260° F.	0.236	0.230	0.235	0.247	...	...	4
140 min. at 260° F.	0.222	0.222	0.225	0.233	...	...	4
K_3	472	488	469	436	...	...	12
Nigrometer reading:							
Red	81.2	81.0	84.4	86.2	...	...	1
Green	83.2	83.3	86.4	88.6	...	...	1
% net volatile	6.0	4.1	5.7	4.4	...	...	1
% DPG adsorption	55.1	42.1	38.1	24.7	...	...	1
				Set VII			
% rebound:							
85 min. at 260° F.	65.6	...	...	...	65.1	...	4
140 min. at 260° F.	64.0	...	...	...	65.0	...	4
Deflection:							
85 min. at 260° F.	0.232	...	...	...	0.234	...	4
140 min. at 260° F.	0.219	...	...	...	0.222	...	4
Nigrometer reading:							
Red	82.0	...	...	...	82.0	...	1
Green	84.3	...	...	...	84.5	...	1
% net volatile	6.5	...	...	...	4.1	...	1
% DPG adsorption	53.5	...	...	...	35.0	...	1
				Set VIII			
% rebound:							
85 min. at 260° F.	65.8	64.2	67.8	...	...	69.2	7
140 min. at 260° F.	66.2	63.4	67.8	...	...	68.3	7
Deflection:							
85 min. at 260° F.	0.239	0.233	0.240	...	...	0.250	7
140 min. at 260° F.	0.229	0.222	0.226	...	...	0.233	7
Nigrometer reading:							
Red	83.0	81.6	83.5	...	...	84.0	1
Green	85.0	84.0	85.8	...	...	86.2	1
% net volatile	5.1	4.2	4.6	...	...	6.0	1
% DPG adsorption	50.4	38.3	33.9	...	...	46.8	1

doubtful, as will be shown below, no exception has yet been found in the case of plasticity. Low rebound and toughness go hand in hand (Figure 5).

Blackness of the black, as viewed by reflected light either in the dry state or when dispersed in oil, has been found to be related to rebound. It is a rather difficult property to measure, but, considering the number of tests made, the average ratings of Table IV are probably reliable. They were obtained with a Nigrometer (*11*), and a high figure represents grayness. It seems obvious that a low-rebound black is a black black (Figure 5).

Volatile matter which is a measure of the oxygen content of the black (*10, 18*) seems to be entirely unrelated to rebound. This is not difficult to believe since there is no rea-

TABLE III. EFFECT OF REMILLING[a]

	Black A	Black B	Black C	Black F	No. of Tests
Regular Milling					
% rebound:					
85 min. at 260° F.	65.1	62.4	65.7	68.9	2
140 min. at 260° F.	63.2	62.2	65.4	68.4	2
Deflection:					
85 min. at 260° F.	0.231	0.220	0.228	0.240	2
140 min. at 260° F.	0.218	0.212	0.218	0.231	2
Vol. rubber/vol. black[b]	1.261	1.345	1.234	1.080	3
One Remilling					
% rebound:					
85 min. at 260° F.	65.4	61.7	65.7	69.2	2
140 min. at 260° F.	63.0	61.9	65.1	68.9	2
Deflection:					
85 min. at 260° F.	0.232	0.224	0.233	0.241	2
140 min. at 260° F.	0.218	0.212	0.221	0.235	2
Vol. rubber/vol. black	1.176	1.200	1.036	1.017	3
Two Remillings					
% rebound:					
85 min. at 260° F.	65.1	62.8	66.0	68.1	2
140 min. at 260° F.	63.0	61.4	64.8	67.6	2
Deflection:					
85 min. at 260° F.	0.234	0.227	0.234	0.248	2
140 min. at 260° F.	0.221	0.217	0.221	0.230	2
Vol. rubber/vol. black	1.159	1.198	0.992	1.012	3
Three Remillings					
% rebound:					
85 min. at 260° F.	65.4	61.9	65.4	67.8	2
140 min. at 260° F.	63.7	60.6	63.7	68.1	2
Deflection:					
85 min. at 260° F.	0.233	0.226	0.233	0.253	2
140 min. at 260° F.	0.222	0.212	0.220	0.233	2
Vol. rubber/vol. black	1.139	1.195	0.967	0.994	3
Four Remillings					
% rebound:					
85 min. at 260° F.	63.0	62.7	64.8	67.6	2
140 min. at 260° F.	62.7	61.6	63.8	67.6	2
Deflection:					
85 min. at 260° F.	0.231	0.226	0.235	0.250	2
140 min. at 260° F.	0.218	0.213	0.222	0.233	2
Vol. rubber/vol. black	1.076	1.128	0.923	0.942	3

[a] A master batch was made of each black, and portions of it were remilled at 24-hour intervals; 24 hours after each remilling, a set of complete tread stocks was milled and an extraction experiment was started. In this way all samples had the same resting period between the last remilling and the final milling or extraction.

[b] Extraction experiment: A 2-gram sample of black master batch was covered with 50 cc. of benzene. Each day for 6 weeks the clear cement was poured off and renewed with fresh benzene. At the end of this time the pellets were dried at room temperature and weighed. Results are reported as volumes of rubber per volume of black. For example,

Initial weight, 2.000 grams containing 0.800 gram black
Weight after extraction 1.336 grams

$$\frac{1.336 - 0.800}{0.800} \times \frac{1.75}{0.93} = 1.261 \text{ vol. rubber/vol. black}$$

son why oxygen content should have any relation to particle size, shape, or any other physical characteristic of a black. It is generally conceded that volatile matter has its biggest influence on such things as rate of cure and adsorptive capacity.

Diphenylguanidine adsorption from benzene (*2*) may be placed with volatile matter as having no connection with rebound. This, too, is not difficult to believe, considering

the profound effect of oxygen content on acid or basic adsorption (*15*, *17*, *18*).

Particle size measurements unfortunately are not available. However, over the broad range of black from Thermax to Super Spectra, low rebound, toughness of uncured stock, and blackness all mean fine particle size. It is possible, then, that within the range of rubber channel black, particle size and rebound may be related. Two other facts may be used to throw some light on this point.

It has been reported before (*4*, *5*, *7*, *16*) that, when a mixture of black and rubber is extracted with benzene, a pseudoequilibrium may be reached beyond which rubber is extracted only very slowly. The data of Table III show that this property is definitely influenced both by type of black and by the degree of milling the rubber has received. It seems reasonable to believe that this rubber is held by forces of adsorption (*3*, *4*) and, if so, the amount held should be a function of the specific surface of the black and hence a function of particle size. Considered in a relative sense, as in Table IV, it appears to agree broadly with per cent rebound (Figure 5).

Finally, it is no doubt possible to go farther in this interpretation of diphenylguanidine adsorption. Diphenylguanidine adsorption should be a function both of specific surface and of the activity of that surface toward diphenylguanidine. The latter is controlled by the oxygen content and is indicated by volatile matter. If there were a quantitative relation between these three quantities (diphenylguanidine adsorption, specific surface, and volatile matter), it would be possible to predict any one of them knowing the other two. In other words, knowing diphenylguanidine adsorption and volatile matter, we could predict specific surface. Although such a quantitative relation is not available, these blacks can be lined up at least qualitatively by such a line of reasoning. Black F has higher volatile matter content than black A. If it had the same specific surface as A it should be more adsorptive. Actually it is less. Therefore, it has less specific surface than A or larger particle size. By a similar line of reasoning other comparisons can be made: F is larger than A, C is larger than B, D is larger than B, and D is larger than E.

Summing up the data of Table IV, therefore, it appears that a black which produces a resilient cured stock (i. e., high rebound) also (*a*) produces a soft uncured stock, (*b*) is a gray black, (*c*) binds a relatively small amount of rubber and consequently has low specific surface, and (*d*) is less adsorptive toward diphenylguanidine than its volatile content requires and hence has low specific surface. The last two relations are distinctly qualitative, and for that reason there is no intention of stating that rebound is a direct measure of particle size.

Ability to Separate Blacks

Entirely apart from its significance or its correlation with other properties, if a test cannot separate blacks clearly, it is of no practical use. This ability to give a clear separation does not depend solely upon the size of the experimental error. It depends rather upon how much larger than the experimental error the total range of readings is.

To be more specific, the total spread in rebound ratings which we find in rubber black is about 20 per cent (Figure 4). The experimental error may be represented by twice the average deviation from the mean, or 1.2 per cent. The total spread, therefore, is seventeen times the experimental error. In order to compare this with the other tests, we may extrapolate the curves of Figure 5 to obtain the

TABLE IV. RELATIVE COMPARISON OF VARIOUS TESTS[a]

	Black A	Black B	Black C	Black D	Black E	Black F	Av. Deviation from Mean
Rebound rating (direct):							
Original mix	100	96.2	102.1	106.4	100.6	105.5	±0.6
After remilling	100	96.6	101.6	...	...	106.6	
Williams rating (inverse)	100	97.8	105.2	111.7	...	...	±3.0
Nigrometer rating (direct)	100	98.9	101.6	105.0	100.6	102.4	±0.8
Bound rubber rating (inverse)	100	95.9	113.0	...	...	115.2	±1.9
Volatile rating (direct)	100	84	92	78	69	107	±8.2
DPG rating (direct)	100	82	71	48	63	97	±3.6
Particle size predicted from volatile matter and DPG adsorption	...	...	Larger than B	Larger than B and E	...	Larger than A	...

[a] These are average ratings taken from Tables II and III. Black A is arbitrarily assigned a rating of 100 and all others are found by proportion, either direct or inverse.

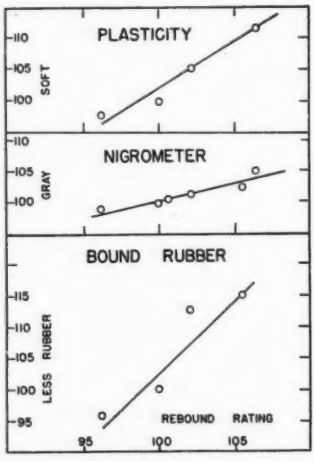

FIGURE 5. CORRELATION OF REBOUND WITH OTHER PROPERTIES (DATA OF TABLE IV)

spread in their ratings corresponding to a spread of 20 in rebound rating as follows:

Test	Total Spread, *A*	Av. Deviation from Mean, *B*	Ratio *A/2B*
Rebound	20	±0.6	17
Plasticity	30	±3.0	5
Nigrometer	11	±0.8	7
Bound rubber	46	±1.9	12

Therefore, of these four tests, rebound seems to give the clearest separation.

Acknowledgment

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A New Revised Rebound Resiliometer

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In recognition of the value of resilience data, the need has been felt for an inexpensive portable and versatile instrument of simple construction and operation. The resiliometer* illustrated was developed to meet these needs.

Description

The accompanying drawing illustrates the simplicity of construction. Part B, the main support or backbone of the instrument, is fitted into and supported by base A. These two parts comprise one unit—the stationary unit.

The second or adjustable unit is composed of the graduated metal tube D, which is attached to rod N (over which the plunger slides) by the connecting member F. The second unit has a sub-unit or trip, which serves as a release for the plunger. With fulcrum at K, pressure is exerted against spring M at bottom of rod J, which, acting through G, releases the plunger for the descent.

The third unit is the plunger E. This plunger descends on the sample sliding over the rod, and rebounding according to the resilience of the sample being tested. The plunger is automatically caught by the trip by returning it to the top of the rod N, the starting position. To assure the greatest accuracy, highest rebound, and to keep the instrument within practical dimensions, the plunger is made to weigh 1 ounce.

The top or movable unit is held in place by set-screws C, by which adjustments are made to accommodate the sample, which may be of any thickness up to six inches.

The scale D is graduated into 100 equal parts. The instrument is of a height to facilitate operation and accurate readings.

The scale at base of stem B is used to measure the hardness, or rather the softness, of sponge rubber by releasing the thumb screws and allowing the 3-pound weight of the top unit to descend on the sample through the rod and observing the deflection at scale B. Using a 1″ test specimen, the deflection or softness can be read directly in percentage.

The instrument is constructed of brass and drill rod throughout, and is completely chrome-plated. The overall height is 18 inches and weight seven pounds. The base is felted to assure protection of the surface on which the instrument is placed.

Operation

The instrument may be placed on a desk or any level surface of convenient height. After the plunger is placed at the top of the rod, the set screws are released, the top unit raised by means of the set screws, and the center of the sample placed directly under the rod. The scale, rod, etc., which move as a unit, are then allowed to descend and the combined weight of 3 pounds is allowed to rest on the sample through the rod. Three pounds is sufficient to prevent vibration of the sample,

* Patent applied for.

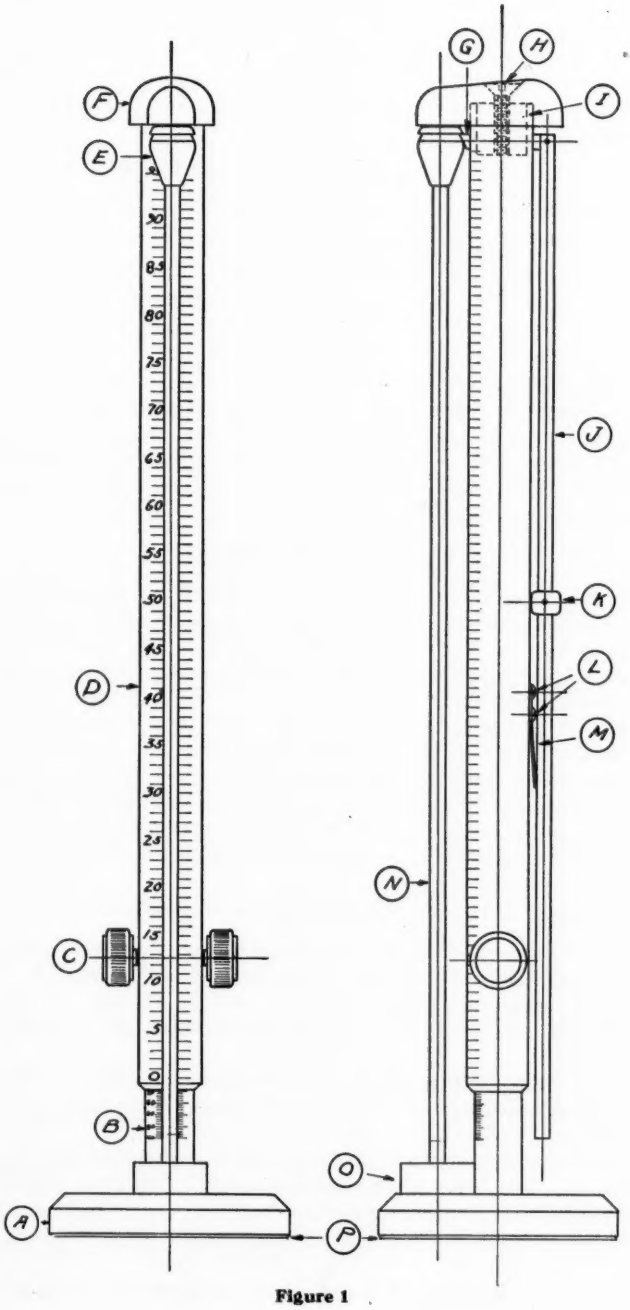

Figure 1

hold it in place, and not cause an appreciable depression where the total weight rests on the sample through the rod. At the option of the operator, the instrument can be so adjusted so that no weight is allowed to rest on the sample being tested. After releasing the plunger by means of the release trip, the reading is obtained by observing the number immediately behind the top of the plunger at the peak of the rebound.

Thickness of Test-Pieces

Up to a thickness of 0.5 inch, the resilience reading increases with increase in thickness of specimen. When a thickness of 0.5 inch is reached, the curve flattens rapidly. Resiliences of pure-gum stock Q of various thicknesses at 70° F. follow:

1/8"	61	1/2"	75
1/4"	70	1"	75
3/8"	72.5	1 1/2"	75

A thickness of 0.5 inch and diameter of 1.25 inches seems the most convenient size of specimen conducive to accurate comparative readings. When comparing competitive samples less than 0.5 inch thick, the specimens should be of equal thickness if the data are to be comparative. When it is not convenient to use a molded sample 0.5 inch thick, discs from regular laboratory slabs may be died out and superimposed to this thickness.

Temperature

Experience with temperature is in agreement with the graphic results of Barnett and Mathews,[1] which show that the percentage resilience increases with increase in temperature. With decrease in temperature the resilience diminishes. Hence results to be comparative should be conducted preferably at a standard laboratory temperature, 70° F.

Owing to the retarding effect of clay and carbon, the accelerator in stocks J and O was increased to obtain the same curing rate of all samples.

Tests were made with specimens 0.5 inch thick by 1.25 inches in diameter. The temperature was 70° F. All samples were allowed to rest 24 hours before testing.

Of interest is the fact that mineral rubber is the only ingredient which decreased both hardness and resilience with increased volume loadings.

Shore Hardness *vs.* Resilience

From the above data, it is obvious that there are four hardness-resilience relations: (1) high hardness-high resilience, typified by compound B; (2) high hardness-low resilience, typified by compound J; (3) low hardness-high resilience, typified by compounds F and Q; (4) low hardness-low resilience, typified by compound G.

It will be noted that the resiliometer measures differences in the state of cure, differences which are not detected by the durometer. Note particularly compounds M and N.

The durometer is in a great many cases incapable of detecting a poorly mixed batch of rubber, since a specimen from such a batch may be overaccelerated and underpigmented or underaccelerated and overpigmented, and still show the same hardness; whereas the resiliometer does measure these shortcomings.

Relation of Resilience to Other Physical Properties

With the same pigment it is obvious that specific gravity, hardness, and modulus

		A	B	C	D	E	F	G	H	J	K	L	M	N	O	P	Q
Rubber	(By volume)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Whiting	(By volume)	25	50	100	150	200											
Mineral rubber	(By volume)						25	100									
Clay	(By volume)								25	100							
Barytes	(By volume)										25	100					
Carbon black	(By volume)														25		
Thermax	(By volume)												25	100			
Zinc oxide	(By volume)															25	
Zinc oxide (on 100 parts rubber by wt.)		5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Sulfur (on 100 parts rubber by wt.)		2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Accelerator (on 100 parts rubber by wt.)		.68	.68	.68	.68	.68	.68	.68	.68	1.4	.68	.68	.68	.68	1.4	.68	.68
Stearic acid (on 100 parts rubber by wt.)		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Hardness (Shore Type A)																	
20 min. cure at 40 lbs. per sq. in. steam		50	59	75	60	80	30	33	50	80	52	75	55	90	70	52	35
30 min. cure at 40 lbs. per sq. in. steam		52	60	77	65	80	32	35	50	80	52	76	55	90	80	52	38
40 min. cure at 40 lbs. per sq. in. steam		52	61	78	80	80	35	36	51	85	52	80	55	90	83	52	40
50 min. cure at 40 lbs. per sq. in. steam		52	61	78	80	82	36	37	52	85	52	81	55	90	85	52	40
60 min. cure at 40 lbs. per sq. in. steam		52	61	78	80	85	35	40	52	85	52	82	55	90	85	52	40
Resilience																	
20 min. cure at 40 lbs. per sq. in. steam		64	57	44	33	24	56	28	60	12	62	35	58	26	34	62	68
30 min. cure at 40 lbs. per sq. in. steam		65	58	45	35	26	63	33	61	13	64	36	62	28	36	63	73
40 min. cure at 40 lbs. per sq. in. steam		64	56	44	34	27	65	36	60	11	65	36	64	30	34	64	75
50 min. cure at 40 lbs. per sq. in. steam		63	54	43	33	25	64	35	59	10	63	35	62	31	31	60	74
60 min. cure at 40 lbs. per sq. in. steam		62	53	42	32	23	63	34	58	9	61	34	60	27	28	59	72

increase with decrease in resilience. It is also obvious that, with the same pigment resilience diminishes with tensile strength and elongation.

Plasticity

Results of tests on smoked sheet milled for various periods follow:

Time of Mastication (Minutes)	Rebound (Percentage)	Plasticity*
0	73	92
15	58	73
20	57	72
25	56	71
30	55	70
40	53.5	69
50	52.5	68
60	51	67

* Measured by the Mooney plastometer.

Cold-pressed samples 1.25 inches in diameter and 0.5 inch thick were used in making the tests on smoked sheet 24 hours after mastication.

If time of mastication is plotted against percentage rebound and plasticity, respectively, the curves are found to be parallel.

Even if sulfur and accelerator are master-batched, plasticity or rebound tests of uncured stock would not seem to be reliable, owing to variation in plasticity of the rubber. This variation is capable of offsetting variations due to pigment dispersion, thereby rendering the results of doubtful value.

Tests on uncured rubber samples do not, therefore, seem to possess the merits of tests made on cured samples, since with the former, tests do not indicate the degree of dispersion of the vulcanizing, accelerating, and activating agents, a very vital shortcoming.

It would seem, therefore, that the range of usefulness of the plastometer and resiliometer in making tests on uncured rubber would be limited to the study of variations due to milling for various periods of time, or in the study of master-batch dispersion, where high loading minimizes variations due to plasticity of the rubber.

Master Batches

Ordinarily master batches, in so far as laboratory tests are concerned, do not secure the attention they deserve, since they are not balanced compounds, and do not contain all the ingredients necessary to secure the proper states of cure.

The degree of master-batch dispersion can be detected by testing cold-pressed unvulcanized samples of the standardized dimensions. Samples 1.5 inches in diameter and 1 inch thick of the following master batches gave the following results.

Smoked sheet	55	33⅓	45	75
Carbon	40			
Thermax		66⅔		
Stearic acid	5			
Sulfur			50	
Accelerator				25
Dispersing agent			5	
Resilience	32	41	53	58
Hardness		No figures obtainable		

Sponge Rubber

By using specimens 0.75 inch thick, or plying up or superimposing discs to this thickness, data may be obtained from sponge rubber. Sponge rubber has approximately the same range of resilience as non-porous rubber, *viz.*, 10–75%.

There seems to be a more definite relation between resilience and hardness of sponge rubber than there is between hardness and resilience of non-porous rubber.

To obtain the most satisfactory criterion in evaluating sponge, both softness and resilience should be linked together; *i. e.*, softness or percentage indentation multiplied by percentage resilience. The results below, obtained by the method outlined in the last paragraph under Description, illustrate this point.

Sample	Resilience (Percentage)		Softness or Indentation Measured as a Percentage of the Original Thickness of Test Specimen		Resilience-Softness Index (Percentage)	Rating
1	58	×	75	=	43.5	1st
2	70	×	25	=	17.5	2nd
3	58	×	22	=	12.8	3rd

It will be noted that No. 3 sample has the same resilience as No. 1, and the other a much higher resilience; yet the R. S. (resilience-softness) index of No. 1 is 3.37 times as great as the former and 2.48 times as great as the latter, indicating in general a much superior sponge. In other words No. 1 is the softest stock with the highest obtainable resilience.

Although there are four softness-resilience relationships, most commercial sponge should fall into the class in which No. 1 exists, *viz.:*

High Resilience-High Indentation (Softness)—Especially desirable when personal comfort is concerned—Armrests, etc. Good aging properties. The other three groups of minor importance are:

High Resilience-Low Indentation (Softness)—Desirable only when a bumper stock should possess high resilience, and it is desired to return the shock or energy. Very limited use.

Low Resilience-High Indentation (Softness)—Extremely soft and soggy—very slow sponge. Desirable only when the utmost softness is desired, and no concern is felt for wearing or aging qualities.

Low Resilience-Low Indentation (Softness)—Extremely hard sponge of poor wearing qualities. Desirable only where a shock absorber is required to carry a sustained load.

Tire-Testing

By removing the top section from the base, and providing a suitable bracket to support this section, tires may be tested with as much facility as an ordinary laboratory sample.

Miscellaneous

Although plasticity tests on uncured rubber mixtures evaluate their working properties in factory processing, and Shore hardness tests help to define pigment loading and evaluate a property differing from resilience, neither test seems to possess the merits of resilience tests for factory control of mixing. Neither will

the combined result of hardness and plasticity tests bring to light the shortcomings of pigment, accelerator, sulfur, and activator dispersion.

Since resilience is a property differing vastly from hardness, etc., the additional data enable the rubber compounder to duplicate competitive rubber goods with greater precision and dispatch. This test offers a link in the long chain of data necessary to evaluate all the physical properties of a rubber compound.

Summary

The following points seem to cover the field of utility for this instrument:

For measuring resilience, a property differing from hardness, modulus, elongation, plasticity, etc.

For greater speed and accuracy in duplicating rubber compounds.

For simplified method for control of factory mixing.

For measuring plasticity, since rubber becomes less resilient and more plastic on prolonged mixing.

For controlling and comparing the quality of finished products.

For measuring the resilience and softness of sponge rubber.

Reference

[1] *Ind. Eng. Chem.*, **26**, 1292 (1934).

[*Note.*—This communication is a revision of an article in the March, 1937, issue of the *India Rubber World.*]

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The Evaluation of Rubber and Rubberlike Compositions as Vibration Absorbers

Apparatus for Automatic Recording

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THE increased amount of information required for structural applications of rubber and Neoprene reveals unmistakably the inability of available test equipment to provide the information most needed by design engineers. On the basis of present tests it is extremely difficult for an engineer to select the material best suited to a given use. He may write his specifications for rubberlike materials much as he would write specifications for steel, and often fails to recognize that the essential differences between the mechanical characteristics of rubber, rubberlike materials, and steel require different methods of evaluation. Rubber goods manufacturers, on the other hand, may not always appreciate the problems of mechanical engineers. The attainment of a common basis of test is important, therefore, and the test equipment described in this paper is offered as a step in that direction. The present paper is limited to factors involved in the evaluation of rubber and rubberlike compositions as vibration absorbers.

It is necessary at the outset to have a clear understanding of the field of application for rubber mountings. Metallic springs have been used for mountings for many years and satisfactorily meet many needs. They possess resilience to a remarkable extent, which under certain conditions is highly desirable, but where oscillation must be absorbed they usually require a shock absorber of one of the conventional types as auxiliary apparatus. The peculiar virtue of rubber or a rubberlike composition as a mounting material is that it has within itself the ability to damp out vibration. This damping implies the conversion of mechanical energy into heat.

We shall assume that the characteristics of a vibrating machine are thoroughly known and that this machine is to be

mounted on a framework in such a way that excessive shocks will not be transmitted to the frame, and oscillations of high amplitude will be prevented. To meet the first condition it is necessary to provide a composition of the proper modulus, which will extend the time element in shock sufficiently to reduce considerably the force transmitted.

To meet the second condition it is necessary to consider the critical speeds of the complete assembly. We will assume that by selecting material with a sufficiently low modulus the critical speeds will be kept low. This simplifies the problem by reducing the required energy absorption to oscillations at low frequencies, a condition naturally favorable to the durability of the vibration-damping composition. At critical frequencies every impulse serves to increase the amplitude of oscillation of the machine; hence, it is at critical frequencies that the vibration damper must absorb the maximum amount of energy.

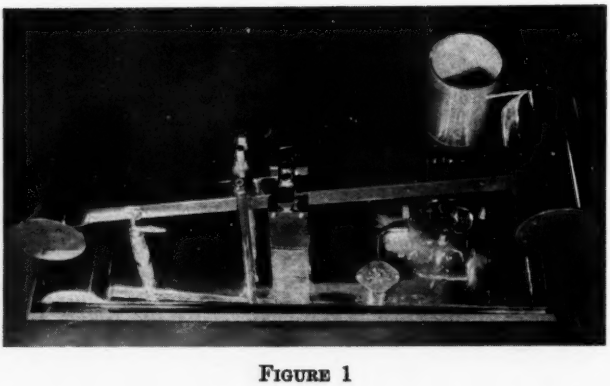

FIGURE 1

No composition for mechanical mountings will be satisfactory unless throughout its life it maintains its original elastic characteristics and form to a reasonable degree. For example, it is desirable that the characteristics of a vibration damper remain reasonably fixed over a wide range of temperatures. However, the art of compounding does not yet appear to have reached the goal where no changes in modulus and damping characteristics occur with changes in temperature. Since complete elimination of temperature dependence is not possible, a suitable tolerance must be allowed in the original plans.

Tolerance must also be allowed for change in form. Obviously a thermoplastic material is not suitable; yet all rubber and rubberlike materials will show a certain amount of permanent deformation under the influence of the dead load. Thus, some slight drift must be expected and in almost all instances can be allowed for in design.

Other factors affecting permanence are principally resistance to oxidation, fatigue, excessive heat build-up, and

deterioration in oils or active chemicals. In considering mechanical fatigue it is obvious that a stock cannot be used beyond a certain allowable stress. This limits not only the original applied load but also involves the extent of motion in vibration. The intensity of the load is related to the question of permanent set, structural disintegration upon repeated working, and extent of heat build-up. The temperature rise during the use of a vibration damper must not be excessive. The limitations of temperature rise are dictated by the resistance of the stock to progressive cure and to deterioration when exposed to air, ozone, and solvents. Oil resistance can be eliminated as a factor by special features of design, which shield the stock from contact with lubricants, but the necessity of shielding from the lubricants may so restrict the design as to limit its suitability. For that reason, there are many instances requiring a stock which is itself inherently oil-resistant.

Mechanical tests must reveal several characteristics. It is necessary to know the static stress-compression characteristics of a proposed vibration absorber. This characteristic determines the allowable load per unit area and is a primary factor in the appearance of drift under a dead load over long periods of time. The test should also reveal the dynamic modulus of the stock as a quality definitely distinguished from static modulus. It is true that the static and dynamic moduli will be very nearly the same if the stock is highly resilient, but high hysteresis causes a difference to appear between the two. Since the dynamic modulus should be considered in properly relating the design of a motor mounting to the frequency characteristics of the motor, the necessity of properly evaluating it should not be overlooked.

The rate of absorption of energy is important. This is the damping feature of the mounting, and since it is a significant factor in choosing rubber, for example, in preference to steel springs, a ready means for its evaluation is extremely important.

Another factor very important in design is the knowledge of the deflections which will result from the application of a given shock load. Although it is possible to calculate the permissible dead load from the static characteristics and to limit the drift by keeping this below certain limits, the question of allowable deformation must be dealt with as a dynamic consideration. Here again hysteresis characteristics and static modulus determine the dynamic hardness. The term "dynamic hardness" is used in this paper to represent the dynamic relationship between impact load and deflection. Thus, a stock with high hysteresis and a given static modulus shows a greater dynamic hardness than a stock with the same static modulus and low hysteresis.

The rapid measure of drift occurring in the first minute of loading may be an indication of the drift to be expected over a more extended period of time, but this does not necessarily follow. However, drift over one period of time is of interest

and such data can at times be an indication of trends which are undesirable. It is necessary to distinguish clearly between the sluggish action which characterizes a high hysteresis stock and the definite plastic flow which is characteristic of undercured rubber or rubberlike materials and thermoplastic materials.

Apparatus

The apparatus which is described in this paper combines measurements hitherto not accessible from simple apparatus, and is a means of evaluating rubber and rubberlike compositions both statically and dynamically. Figures 1 and 2 illustrate the construction.

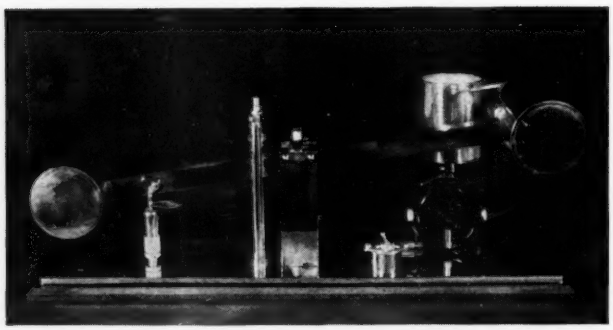

FIGURE 2

The machine consists of an unbalanced lever with a 20-pound weight on one end and a 10-pound weight on the other, pivoted on a knife edge at the midpoint of its length. The test piece is a small rubber cylinder 0.75 inch in diameter and 0.5 inch high.

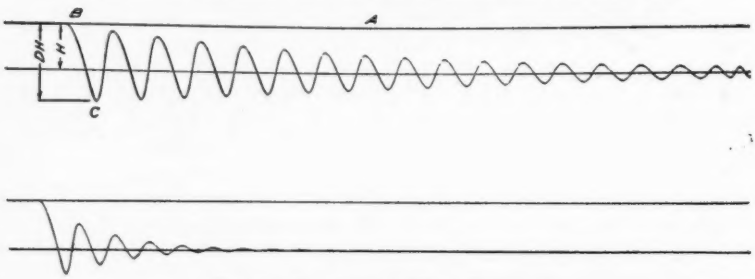

FIGURE 3. ACTUAL TEST RESULTS

During the test this is compressed between a stationary horizontal surface and the upper surface of the unbalanced lever in such a position that the compression of the test specimen resists the tendency of the 20-pound weight to fall. Thus, if the heavy end of the lever is lifted and then released, the test specimen is subjected to a shock load and is distorted beyond the static equilibrium position. In this way an oscillating system is established and the 20-pound weight rises and falls while the test specimen goes through various degrees of compression. Each oscillation

is smaller than the previous one, owing to the internal friction or mechanical hysteresis of the test piece, and eventually the lever comes to rest. A hook shown in the left foreground of Figures 1 and 2 secures the weight initially in a definite position and is adjustable in height. By releasing the hook, the weight falls from a predetermined height, and the energy input is determined by multiplying the height through which the 20-pound weight falls by the number of pounds of unbalanced weight.

A pen mounted on the heavy end of the lever traces a record on a revolving drum which is driven by a synchronous motor. Thus, the amplitude and frequency of the oscillations can be permanently preserved for analysis.

TABLE I. COMPOUNDS TESTED

	No. 1	No. 2	No. 3
Smoked sheets	100.	100.	100.
Zinc oxide	5.	5.	5.
Channel black	40.	40.	...
Soft carbon black[a]	...	20.	...
Stearic acid	1.5	1.5	1.5
Pine tar	6.	6.	...
"D" Phenyl-β-naphthylamine	1.	1.	1.
Zenite B[b]	0.8	0.8	0.8
Sulfur	3.	3.	3.
	No. 4	**No. 5**	**No. 6**
Neoprene type E	100.	100.	100.
Extra light calcined magnesia	10.	10.	10.
Channel black	...	25.	50.
FF rosin	5.	5.	5.
"D" Phenyl-β-naphthylamine	2.	2.	2.
Sulfur	1.	1.	1.
Zinc oxide	5.	5.	5.

Press cure:

Compounds 1 and 2, 40 minutes at 40 pounds' steam pressure (141.5° C.)
Compound 3, 25 minutes at 40 pounds' steam pressure (141.5° C.)
Compounds 4 to 6, 40 minutes at 60 pounds' steam pressure (153° C.)

[a] P. 33 was used.
[b] 90 per cent zinc salt of mercaptobenzothiazole–10 per cent di-ortho-tolylguanidine.

TABLE II. RESULTS OF TESTS

Compound	Dynamic Hardness	Static Hardness	Amplitude of Sixth Rebound	Resilience, %	Shore Durometer Hardness
3	138	87	49	56	38
4	128	86	11	13	41
1	119	84	2	2	52
2	108	77	2	2	57
5	98	69	3	5	56
6	71	53	1	2	74

Figure 3 (upper) is an actual test result obtained from a fairly resilient composition. Line *A* is the zero reference made by lowering the pen to the surface of the drum and allowing the drum to rotate through one revolution with the pen in a stationary position. On the second revolution the heavy end of the lever is released at point *B*. Point *C* represents maximum compression of the pellet, and the distance from *C* to the line *A* is a measure of dynamic hardness. The line *BC* is a graphic indication of the response of the test specimen to an impact load. Subsequent oscillations indicate the rate at which the impact is absorbed. If successive amplitudes rapidly diminish, the composition is one which will not

readily support vibration at critical frequencies. The rapidity with which the oscillation record crosses the time axis is an indication of frequency and is related to the value of the dynamic modulus under the given test conditions.

Figure 3 (lower) is an actual test result obtained from a composition with much lower resilience.

If a stock has a tendency to drift under a dead load, this can readily be detected by allowing the drum to rotate through two or three revolutions when the lever is resting in its static equilibrium position. Qualitative information of this sort may often be useful.

Applicability

To illustrate the applicability of the test to the evaluations of a variety of compounds, static and dynamic characteristics of six rubber and Neoprene compositions (Table I) are given. Shore durometer hardness is also given to provide a rough basis of comparison with present test methods (Table II).

Dynamic hardness, static hardness, and the amplitude of the sixth rebound are given in arbitrary units of hundredths of an inch as measured on the autographic record. The ratio of the amplitude of the sixth rebound to the original elevation of the 20-pound weight is arbitrarily taken as the figure for the resilience of the stock.

There is no reliable correlation between Shore durometer hardness and dynamic hardness as evaluated by this test. The durometer makes a surface test, whereas the apparatus described herein makes a volume test, which is obviously in closer agreement with the loading to which a motor mounting is subjected.

Compounds 3 and 4 have approximately the same static hardness. Compound 4, however, shows noticeably greater hysteresis since the resilience is lower. This factor contributes to the lower measured dynamic hardness of 128 as compared with 138 for compound 3. Compounds 1 and 2 are rubber stocks having high hysteresis and are presented to show the differences in hardness revealed by this test both dynamically and statically. Compounds 5 and 6 are Neoprene stocks.

The machine can be designed for use either in an oven or a refrigerator by mounting the recording mechanism outside of the box and by providing a remote control of the weight-release mechanism. By such an arrangement tests of a given test piece can be made over a wide range of temperatures. If a stock is reasonably oil-resistant, its characteristics before and after an immersion test can be compared. The machine can also be used as a valuable auxiliary to one of the existing fatigue machines, to evaluate a test piece periodically throughout the duration of a life test.

Summary

The equipment is simple and foolproof. It provides an autographic record in a few seconds, from which can be evalu-

ated dynamic hardness, dynamic modulus, internal friction, static hardness, and drift.

It can be used to test rubber and rubberlike compositions over a very wide range of temperatures—for example, from −40° to 150° C.—for testing compositions which have been exposed to solvents or gases, and in conjunction with a fatigue machine for evaluation at various stages in a life flexing test.

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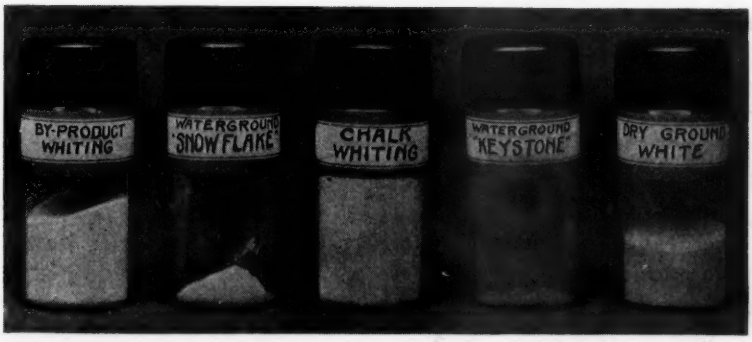

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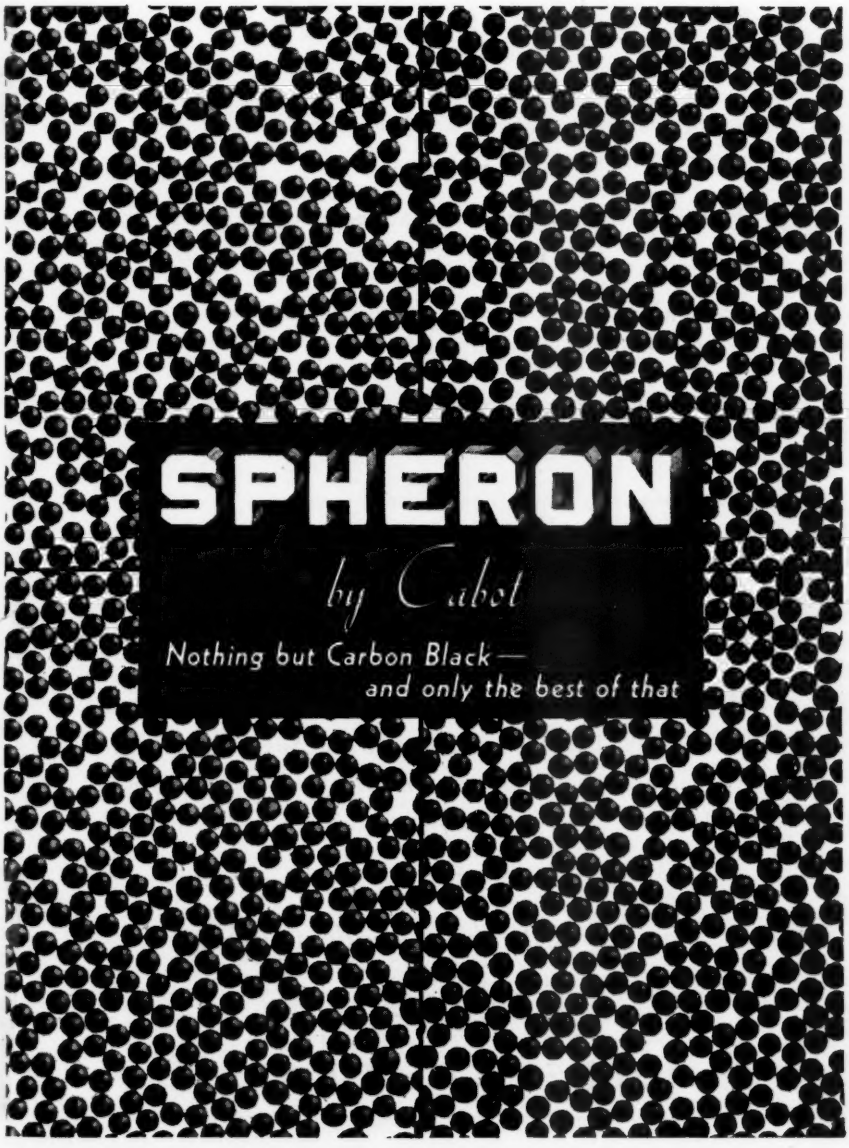
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October, 1937

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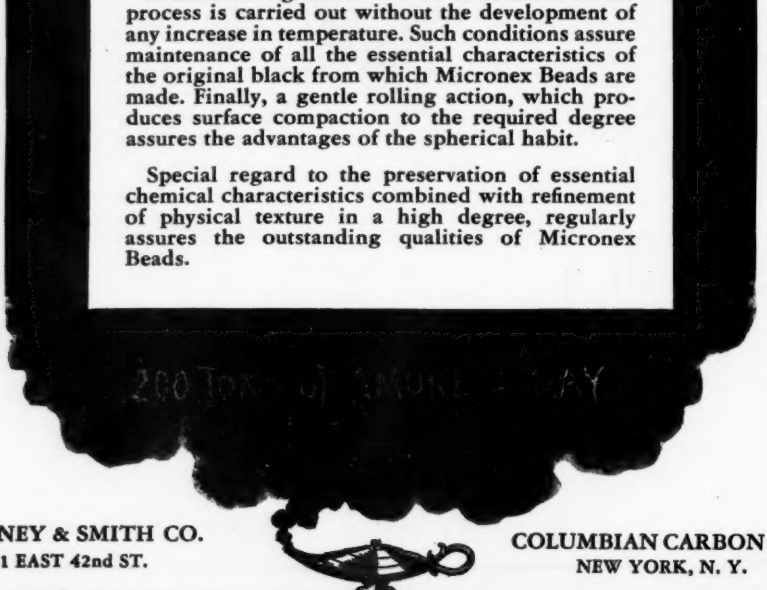

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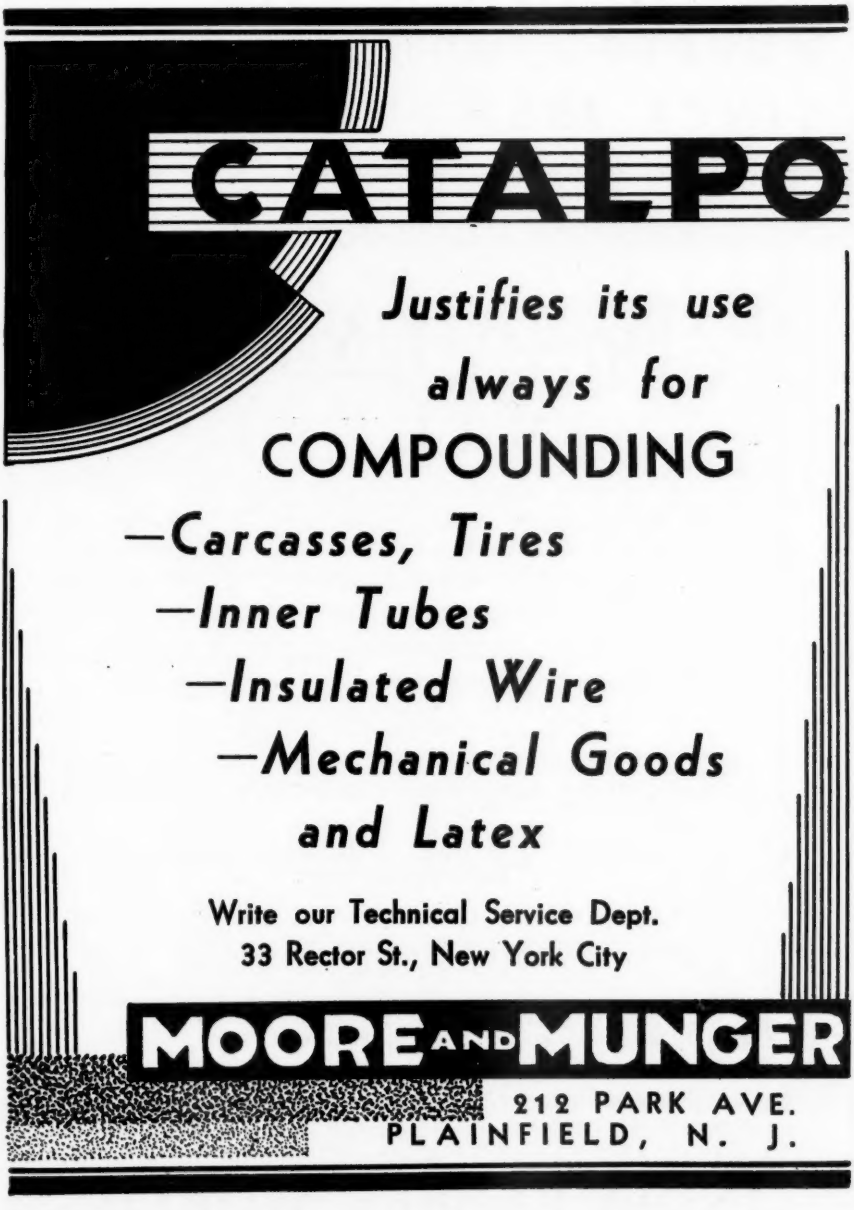
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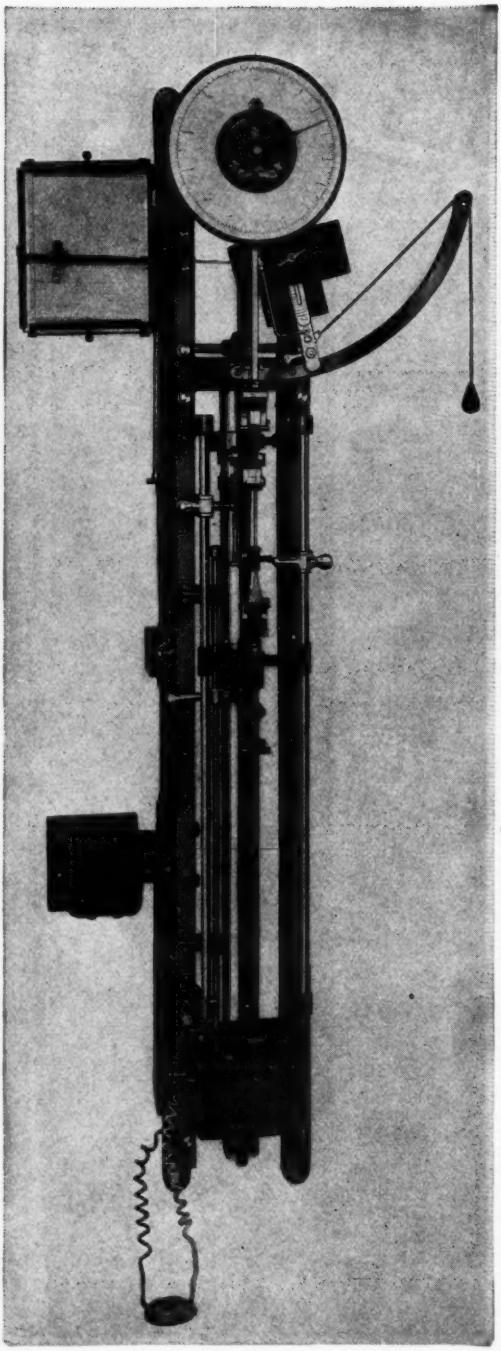

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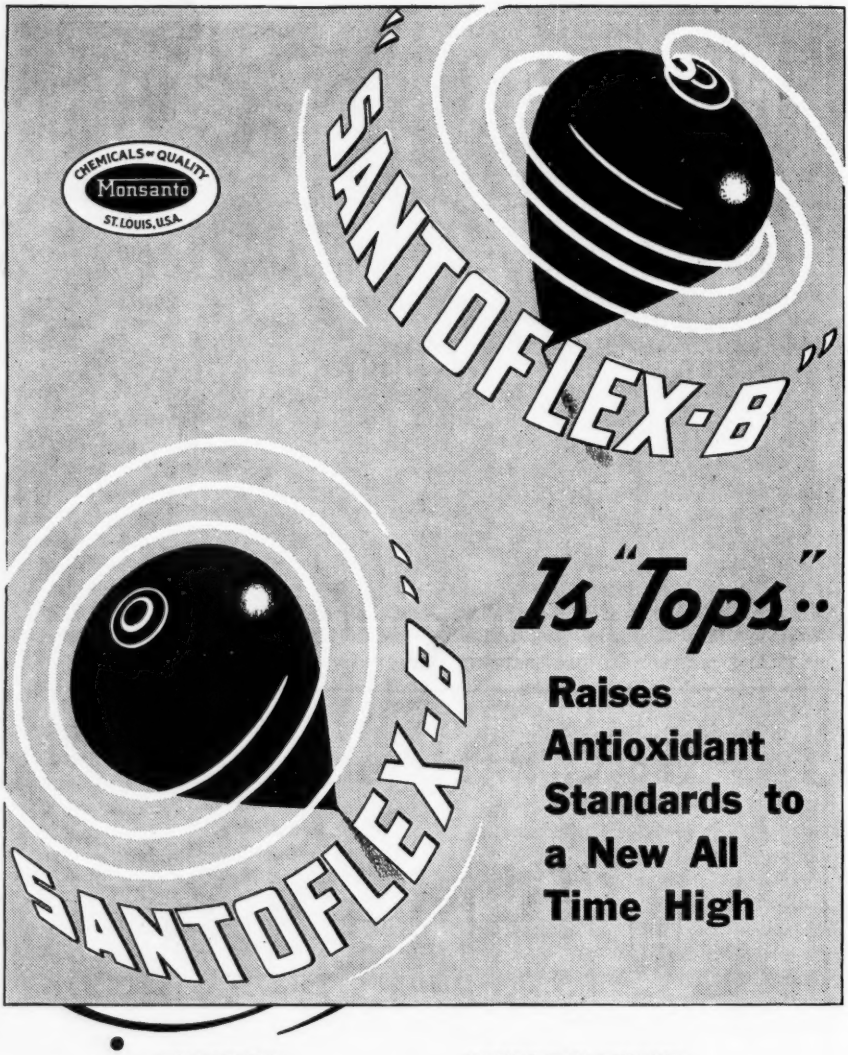

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